RESEARCHES ON CELLULOSE
IV.

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(1910-1921)

(VOLUME IV. OF THE SERIES 'CROSS AND BEVAN')

BY

CHARLES F. CROSS AND CHARLES DORÉE

*WITH FOUR PLATES AND TWELVE DIAGRAMS
IN THE TEXT*

PREFACE

In this volume we have shaped our basis of constructive criticism to meet the rapidly changing aspect of the section of science included in the comprehensive term 'Cellulose.' We review a period of eleven years : a period of great scientific development coupled with the intensive technical output occasioned by the war.

The authorship will remind our readers of the death of Edward J. Bevan, who, for forty years, took part in the research work upon which the previous volumes were founded.

We have in view the task of re-writing the original volume ('Cellulose,' 1895), but still defer the undertaking pending a more definite general agreement upon the fundamental aspect of 'Constitution,' which, we have to admit, is still a problem, as the contents of this volume endeavour to show.

In the meantime, this critical survey is a record of progress and, with the preceding volumes, an adumbration of the comprehensive Text-book, which in due time will replace the work of 1895 which, though now ancient, is not entirely out of date.

We have to express our thanks and acknowledgments to the following publishing societies, and to the authors of papers, for permission to reproduce the diagrams and illustrations which we have given : to the Royal Society for Fig. 1 and the photographs on Plate I. (W. L. Balls) and Plate II. (W. Robinson) ; to the Biochemical Society for the photographs on

Plate IV. ; to the Chemical Society for the curves shown in Fig. 4 ; to the Society of Dyers and Colourists for the photograph on Plate I. (*a*) and Fig. 3 (S. J. Lewis) and also for Fig. 12 ; and finally to the Manchester Literary and Philosophical Society for allowing us to reproduce the paper of H. E. Williams with its illustrations ; also to Courtauld's Ltd. and Mr. S. S. Napper (Research Chemist) for permission to publish the note of researches on specific volumes, pp. 22-30.

We are further indebted to our friend, Mr. J. F. Briggs, for the preparation of the Index.

C. F. CROSS,

3 New Court,
Lincoln's Inn, W.C.

C. DORÉE,

Chemistry Department,
Borough Polytechnic Institute, S. E.

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INTRODUCTION

THE series of 'Researches,' of which this is the fourth, are intended as supplements to the original volume on 'Cellulose' (1895). It was then recognised that the subject was in active growth, and from the present retrospect it is seen to have been phenomenal. This is sufficiently evidenced by the well-known text-book of C. Schwalbe, 'Die Chemie der Cellulose' (1911), and by the more recently published monograph of E. C. Worden, 'The Technology of Cellulose Esters' (1921), with a bibliography recording the research work of 55,000 investigators. Another feature of development of the literature of the subject is the recognition of 'cellulose' as a representative or prototype of colloidal matter, and hence it is a prominent sectional subject of the important serial publications, 'Kolloid Zeitschrift,' 'Kolloid Chemische Beihefte,' of such technical journals as 'Le Caoutchouc' (Dubosc, Paris), and of the important reviews of Colloid Chemistry, published under the auspices of our British Association Committee and the Department of Scientific and Industrial Research.

Certain of the 'learned' and technical societies have constituted special 'Cellulose' sections, e.g. the American Chemical Society; and in Germany the publications of the Verein Papier Techniker are necessarily devoted in the main to cellulose problems.

In our own country the Textile Institute has been founded, and its journal contributes records of research work in this field.

A research association has been formed in connection with the cotton industry, and it is evident that the chemistry of cellulose is a main objective of the scheme of research. The Fine Cotton Spinners Co. of Manchester, our leading corporation in this industry, has organised its own research laboratory, and some mention is made of this in the text (p. 205).

Similar research associations are projected in connection with the flax and jute industries. The Papermakers' Association has already constituted a research section; the laundry industry also. The further exploration of the unlimited field of problems connoted by 'cellulose' is their necessary and, in fact, main object.

In this state of progress and development it might be questioned whether the publication of the present review is justified. On the other hand, critical evaluation of this abundant output of research publications is more than ever necessary in order to keep really fruitful progress in the forefront, to aid the worker in this field by judicious selection from the mass of material presented to him, and to inform those who are interested but have not the same opportunity of special study. As a mere review it could have no other value than that of an impressionist survey. We find, however, that we are still able to develop some aspects of the subject, which have been tentatively dealt with in the preceding volumes, by contributions of new matter. This new matter, included in the text, also involves a basis of criticism of the researches of others : a criticism largely of appreciation, with some questioning of conclusions which appear to us based on inadequate conceptions of organic function, and with some indications of a broader basis of outlook and correlative extensions of the field of investigation.

RESEARCHES ON CELLULOSE

IV

CHAPTER I

GENERAL

In reviewing the research work of the last decade it is necessary to remind ourselves of the three independent aspects of 'Cellulose' as a subject of investigation which give definition to the aims of sectional workers and their contributions, which on the other hand are necessarily interdependent, but are seldom found joined in a balanced perspective of criticism.

(1) Cellulose as a colloidal substance 'organic' in function and assuming, correlatively, highly specialised and infinitely varied structural forms; further, without doubt, retaining after separation from the plant, characteristics of reactivity impressed by the conditions of vital origin; a substance to be investigated *as it is*, therefore rather by physical methods, including in the broader sense of the term, the methods of the physiologist and the histologist.

(2) Cellulose, as a chemical individual, to be investigated as such, therefore by the methods of the systematic science, which in a sense are self-contained, and detached from the complications of the wider outlook.

(3) 'Cellulose' under transformation : (*a*) by 'natural' processes to massive complexes such as the peat-lignite-coal series, and to the analogous, but diffuse forms of humus ; (*b*) by laboratory process, such as destructive distillation ; (*c*) by bio-chemical processes of 'fermentation' by which the celluloses are attacked, and resolved : in the one direction to proximate products, in the other to ultimate products of least molecular weight (C_3 to C_1).

To these sectional aspects it would be proper to add a fourth, which comprehends the industrial uses of cellulose, and their complex technology. This connotes a vast field of many-sided interests ; of technical processes based on exact knowledge and control, therefore scientific, though developed through empiricism ; also of prospective discovery, all of which are elements in the perennial attraction of the subject-matter to successive generations.

This section is, however, too vast to be imported, otherwise than by mention, into the present survey : which, moreover, must of necessity be rather impressionist, than systematic or exhaustive.

But it is mentioned with the particular purpose of directing attention to the undoubted fact that much of the progressive research work in this field has been directly inspired by the problems, difficulties, and sometimes the positive aspirations of the technical industrial world.

Of the three main aspects, or dimensions of the subject-matter adopted by way of simplifying the present essay, it must be recognised that the work of the systematic chemists under (2) continues to contribute the most important advances in our exact knowledge of cellulose. While this section comprehends the general study of reactions, its main objective is in the field of the quantitative resolution to proximate products, more especially those (carbohydrates) of known constitution and configuration.

The cellulose-dextrose relationship has been recognised for a century (Braconnot, 1819) and assumed to be quantitative after the work of Flechsig (1882), who claims to have obtained the sugar in large yield, and identified it as dextrose; the investigation extended by Ost, and later by Willstätter, in the light of the modern exact and comprehensive knowledge of the sugars, it is now commonly accepted that the assumption has been justified by proof.

The most recent critical studies simply affirm 'that cellulose is closely related to dextrose, since it yields the latter quantitatively on hydrolysis' (H. Hibbert, 'The Constitution of Cellulose,' 1921).

These resolutions following direct interaction (ester-formation) with acids (H_2SO_4, HCl) as first stage have been extended to the esters (acetates) and ethers (methoxides and ethoxides); the ultimate products, derivative carbohydrates of known configuration, more exactly 'define' the stages of resolution. The results generally confirm the conclusions previously established and appear to independent critics to warrant the statement that 'cellulose is thus nothing more than a polymerised dextrose glucoside of dextrose' (Hibbert). On similar lines of critical treatment of the quantitative data of starch resolutions the long established relationship of cellulose and starch as analogues is very precisely defined, 'starch representing a polymerised form of lævoglucosan.'

Between these two individuals, or rather groups of individuals, which in a sense dominate the vegetable world, representing extreme divergences both as forms of matter and in function, there come the wide range of infinitely differentiated hemi-celluloses and pectins, characterised by physical properties intermediate between those of the extremes.

The systematic chemistry of to-day would no doubt apply the generalised conclusion as to constitutional type, and regard these intermediate products of plant life as representing

variations of the prototypes ; that is, they are polymerised monoses, of which it remains only to establish the order and degree of polymerisation.

Further, the modern chemistry of the carbon compounds which identifies the individuals in terms of structure and configuration presumes always the constructive end of synthesis, and we note this as generally implied in the groups of investigations of the celluloses which we shall record later, in some detail, and expressly claimed to be now brought within measurable distance by the author of the critical general review above mentioned (Hibbert).

The prospect of synthesising the monoses to colloidal complexes rests for the present on this vague, because indeterminate, basis of polymerisation, a process or group of processes which lacks the directive control characteristic of interactions of specifically reactive groups or residues, upon which the logical development of 'organic' chemistry largely depends.

On the other hand, the classic constructive work of Emil Fischer in a parallel region of colloidal products is without doubt taken as an adumbration of results attainable : with due recognition of the distinction between the simple amino-acids and the simple sugars in regard to laboratory methods of building up the polypeptides and polysaccharides respectively. The polypeptides also confirm the general assumption that with increase of molecular dimensions there is a development *pari passu* of the physical characteristics of colloids. We must therefore recognise that the 'pure chemistry' of cellulose rests, in its detachment, on a solid basis of progressive achievement, buttressed by many inferential supports, and the workers appear to be justified in excluding such complicating issues as between questions of actual origin, visible structure, and organic functions.

On the other hand, the chemists' generalised picture of the cellulose-starch groups are diagrams, and in regard to realities,

almost as sterile of suggestion of the cause of the specific activities of the substance, as of particular features of their reactivities. In general criticism of any constitutional picture of a polymerised monose, or immediate anhydride derivative we note :—

(*a*) The wide divergence of the properties of cellulose from those of starch, and of both from monoses or their anhydrides, and special features of divergence and differentiation not to be explained as a function of degree of polymerisation.

(*b*) The resistance of cellulose to extreme action of alkalis and to certain acid treatments specifically calculated to attack a condensed aldehyde-oxide complex, more especially the action of bisulphites at 135° to 150°.

In regard to the former, the normal (cotton) cellulose quantitatively survives the alkali-cellulose-xanthate- (viscose) cellulose cycle, and even the 'fusion' process of Lange (NaOH at 180°), so far that the process has been proposed as the basis of a laboratory method of estimating 'cellulose.'

(*c*) Cellulose has characteristics of reactivity *sui generis*.

(1) It is affected and modified by any and every treatment with reagents, inclusive of water.

(2) It is transformed integrally by chemical reaction obviously limited to partial, and sometimes, fractional effects.

(3) All its most characteristic reactions are 'continuous,' the quantitative changes show no definite molecular stages, and the accompanying modifications of physical properties are similarly gradual and progressive.

(4) In the ester reactions (notably with the nitrates and acetates) the suppression of the OH groups as such, and the entrance of 60 to 70 per cent. of its weight of acid radicals take place without seriously modifying the properties of the original as a structural colloid.

(5) Cellulose is sensitive to all forms of energy, or the energies, light, heat, electricity ; and has been shown to be

profoundly affected in structure and constitution by treatments of a purely mechanical-physical order.

(6) Cellulose has long been known to be resolved under bacterial action to ultimate products, and certain of these processes have been systematically studied (Macfadyen-Omeliansky). By later researches, these actions have been brought under control, such that the normal celluloses are treated in massive quantity, and resolved in relatively short periods of time, to ultimate products.

These processes, as industrial operations for the production of acetic acid and alcohol, are similar in character to the starch fermentations of the brewer and distiller, but with the distinction that the intermediate transformation to water-soluble products (of hydrolysis) is not a necessary stage in the case of cellulose. The mechanism of the ' fermentation ' appears to be essentially a direct break-down of the solid fibrous substance determined by the bacteria attaching themselves to the surface and inducing the effects observed in the cellulose system, i.e. the reacting unit mass, by transmission.

The points thus enumerated in critical comment on the too positive conclusions of systematic chemistry are the subject of more detailed notice, as particular contributions, in the succeeding sections of the present treatise.

There remains to be brought into evidence in this general review, some considerations of less definite import, but with a bearing on the wider problem considered, *a priori* and with reference to the other complementary aspects of the subject-matter. Whatever view may be held of the constitution of ' cellulose ' any particular cellulose must be heterogeneous and no two portions of any mass of cellulose can be identical.

There is, nevertheless, a prevailing quantitative uniformity in the data of reactions both of synthesis (derivatives) and of resolution.

The evidence, or measure of this uniformity, involves the

difficult question of a statistical, or mass-average, as against the predominant method of interpreting reactions in terms of the molecular reacting unit. In the laboratory study of carbon compounds, the actual masses of reagents interacting are of incidental moment : though they become primarily important when translated into industrial processes for the manufacture of products, in reference to the particular objective of economic realisation. The central point involved is that the vast majority of carbon compounds are studied and defined on the generalised basis of accepted theory : and a reaction defined by identified products is formulated, without discussion, in the ideal terms of molecules. Reaction in the cellulose region cannot be so interpreted : we have no measure of the reacting unit ; and in passing from a cellulose to derivative products we have no criterion of accompanying physical changes of which the obviously important are those of energy and volume. The measurement of these factors of constitution is beset with extraordinary difficulty, and although progress has been made in the accurate determination of specific volumes we know so little of the solid state, especially that which characterises colloidal aggregates, that the data can only be applied to determine particular points of relationship.

In the starch-maltose-dextrose series these complications are lessened to the extent that the volume relationships of the products (water-soluble forms) have been measured with accuracy by H. Brown, and the thermal data of an important change have been determined.

From a consideration of these data we have called attention (1) to the increase of specific volume in passing from the original colloid to the ultimate monose, and (2) the large difference in thermal effect of the 'hydrolysis' of starch and that of cane sugar ; *and* the suggestion therefore that the generally accepted pictures of starch transformation may require complementary interpretation in terms of synthetic changes within

the starch system.   This is a suggestion which could not arise
on the polysaccharide view of the actual constitution of the
starch-cellulose groups.   On the other hand the suggestion is
a more particular inference from the study of several reactions
in the cellulose series, and notably from the observed mechanism
of bacterial resolution : in which the cellulose functions rather
as a liquid system, transmitting disturbance of equilibrium.

Moreover, if this suggestion is applied in dealing with the
apparent uniformity of reaction in cellulose, necessarily ob-
served in mass or in masses, and requiring the control and
interpretation of statistical as opposed to molecular data, it ex-
tends to the interpretation of accompanying features of reaction,
thus :—

(*a*) Effects which are in many cases disproportionate to the
actual causes : as in the 'oxycellulose' transformations with
calculated small proportion of 'active oxygen,' e.g. the par-
ticular oxycellulose investigated by S. J. Lewis for volume
changes in water and toluene (p. 26), the specimen being
prepared by treatment with hypochlorite oxygen in the ratio
$HClO : 3 . C_6H_{10}O_5$.

(*b*) After partial reaction the cellulose shows integral re-
sponse to induced reaction (hydration) as in the particular
modification of the xanthate reaction described and discussed
on p. 104 ; and also, through its synthetical derivatives, which
resist resolution to fractions under the action of solvent re-
agents, the original complex manifests integral modification.

It is difficult to marshal these points of direct and inferential
bearing in the order of a systematic proof: but at the moment
we only seek to establish as a proposition that the polydextrose
views of constitution are too positive and beyond the warrant of
a critical comprehensive survey ; the alternative is the reasoned
agnostic position which leaves open all the contributing avenues
of observation, experience, and exact knowledge of the workers
who investigate 'cellulose' objectively, and to whom the results

of the systematic chemist are only one aspect of the subject-matter.

Moreover, the systematic chemist's 'cellulose' is cotton cellulose, or rather the substance of bleached cotton, and it is an obvious criticism of many investigators in this field that they ignore the essential variability of the product. A 'chemical filter paper' and a 'surgical cotton wool' are not constants, and no systematic researches should be undertaken with any specimen of cellulose not fully characterised either as normal or definitely varying from the normal.

In the same order of criticism the conclusions from systematic quantitative research upon cotton cellulose are not applicable to other types, such as the cellulose of pine woods, or esparto grass, and the investigations if extended to more markedly differentiated types would gain much in general value : would also probably disclose constitutional points subversive of many of the too facile conclusions of workers in this field.

In regard to derivative types, also 'natural' products, notably the lignocelluloses and cutocelluloses, it appears that workers sometimes ignore the records of researches, appearing to be unaware that there is a bibliography going backwards fifty years, or that exact knowledge has reached a definite level in relation to which their contributions are 'weighed in the balance and found wanting,' and so much so that formal *criticism* would rather obscure the fact.

Notable instances occur in German literature in the treatment of the 'lignone' problem. The product obtained by Czapek, denominated 'Hadromal,' and assumed to be so related to the parent lignone complex as to characterise it integrally and constitutionally, appears to be one of a vast number of derivatives obtainable by natural or by laboratory processes, of little defined relationship to the parent lignone. Klason's researches in the constitution of wood lignone, noted later

(p. 170) as an important contribution to the subject, take no note of facts such as (1) our adoption in 1886 of the unsaturated aldehydic side chain, as a key position of the lignone complex, explaining the mechanism of the bisulphite resolution of the lignocelluloses to cellulose and sulphonated lignone derivatives ; (2) the critical selection and adoption of the lignone complex of the jute fibre, as the prototype of the group ; (3) the systematic attempts to convert this complex by laboratory process into benzenoid derivatives, with uniformly negative results which ruled out of consideration any constitutional formula, including or based upon a group of definitively 'aromatic' type such as coniferyl alcohol. There were many *a priori* suggestions of such relationships in the older literature (1880-90) which we took into account, in the form of working hypotheses, in our investigations. Having disposed of them so many years since we have been surprised at their revival. We have not thought it necessary to criticise Klason's work. We have rather waited for his independent general confirmation of our results, after passing through analogous experiences.

CHAPTER II

PHYSICAL PROPERTIES AND RELATIONSHIPS

IN the order of treatment set forth in the last chapter, it is necessary to give some account of researches which deal with the 'actual' cellulose in its countless forms or modifications as distinguished from the chemist's 'cellulose,' which is pictured on the one hand, in terms of resolutions and decompositions, on the other, of synthetical derivatives. The 'actual' cellulose is a substance with a structure, visible or external; a colloid, occupying a definite volume *qua* substance, an apparent volume *qua* structural configuration; with properties measurable in relation to force, and in relation to the various forms of energy.

It is clear that the more important 'cellulose industries' are concerned with the 'actual' or physicist's cellulose, and have reached an advanced stage of technical perfection independently of any claims of 'science' to have supplied the formal basis of first principles for their control.

It is, however, articulately recognised that 'science' has a large and legitimate field of exploration in investigating cellulose structures : such investigations will necessarily merely re-edit much of the history of empirical progress, but must contribute to future progress not only by reducing the ultimate factors of industrial processes to exact expression, but by stimulating the imagination of workers in leading them into the sub-sensible region of ultimate cause and effect.

Much of this matter is outside the scope of the present essay : in fact we have to limit our treatment to such sections or aspects as are strictly complementary to the main theme, which is the chemistry of 'cellulose' as generally accepted. The basis 'generally accepted' would almost appear to rule out the complementary aspects of structure, for to the workers under section (2) of Chapter I., p. 1, cellulose is a 'chemical individual' which will be synthesised in due course by laboratory process, following its exact definition under a structural constitutional formula.

Against this somewhat violent view the following considerations have to be urged :—

(1) The structural properties of an original 'cellulose' are maintained in its (normal) synthetic derivatives (nitrates, acetates, and xanthates) : a degraded cellulose forms derivatives relatively degraded *qua* structural properties.

(2) Cellulose is constitutionally changed by any and every treatment to which it is exposed : as a secondary consequence no two masses of cellulose are constitutionally identical.

(3) In the passage from a cellulose to any derivative it cannot be affirmed that there are no volume changes involved. Volume changes probably occur, and may be those of ultimate constituent groups. Since cellulose appears to 'fix' energy externally communicated, and in various forms, its intrinsic energy is not invariable : the variations may be those of the ultimate constituent groups, but more probably are those of proximate configuration.

Other considerations will be developed in order of treatment ; but these are sufficient to justify a prominent treatment of subjects comprised in section (1) of the Introduction. At the same time, we repeat, such treatment is narrowly delimited to matters complementary to the main theme.

We proceed to notice a selection of researches dealing with fundamental points.

INVESTIGATIONS ON TEXTILE FIBRES.

W. HARRISON (Proc. Roy. Soc., 1918 (A), **94,** 460).

Observations of the double refraction of cotton fibres show that the cellulose substance in the natural state retains the internal stresses impressed on it during growth, of which the main characteristic is that of extension of an (originally) spherical unit or cell.

Artificial fibres prepared from cellulose solutions show strong double refraction, and under the action of stress, heat, and moisture, behave similarly to cotton fibre. Stresses externally applied are removed by wetting, and the effects are limited to changes of external form, but the stresses accompanying the original shaping of the plastic colloid are not affected, and are therefore probably due to the more fundamental cause of volume change.

The internal stresses in cotton are represented by a negative pressure along the axis, or a positive pressure in all other directions.

Observations of cotton under the action of cuprammonium solution show that portions of the fibre are relatively resistant and resistance is marked by the persistence of the original optical characteristics. Fibres from the cuprammonium solution show double refraction only under stress, but the effect persists after removal of the stress.

The author discusses these properties of textile fibres in relation to processes of manufacture and ' finishing ' treatment, and shows that investigations of this order are necessary to establish a scientific technology.

*   *   *   *   *   *   *

There are two points in the above which may be emphasised: (1) the fibre colloid is capable of retaining permanently the effect of stress, and (2) where this is permanent it is probably accompanied and determined by volume changes.

In an earlier work, 'Investigations on Mercerised Cotton' (*J. Soc. Dyers and Col.*, 1915, **31**, 198), W. Harrison has also made an extensive use of physical methods of attack in dealing with the problems associated with mercerisation. He succeeded in photographing the fibres under the ultra-microscope during solution in solvents and employed polarised light to diagnose the direction of strain in the fibres. His conclusions are: 'that the compounds formed in the reaction between cotton and caustic soda are probably adsorption compounds; that mercerised cotton is cellulose in a higher degree of dispersion than in ordinary cotton; that the shrinking and untwisting of cotton fibres during mercerisation are due to strains within the fibre, which are liberated when the cotton is softened by the caustic soda; that the lustre of mercerised fibres is mainly due to the fact that the fibres have smooth surfaces in comparison with fibres unmercerised and mercerised without tension; that the section of all fibres has an influence on the lustre, particularly if such fibres have smooth surfaces.' The original should be consulted for photographs demonstrating these various points.

STRUCTURE OF COTTON FIBRE. DAILY GROWTH RINGS OF THE CELL WALL.

W. L. BALLS (Proc. Roy. Soc., 1919 (B), **90**, 542).

The author's previous investigations in this field led him to recognise special features of certain reactions to be subsequently described (p. 104), under which fibrous celluloses are hydrated to a maximum without distortion. Cotton fibres thus hydrated show a 40 to 50-fold increase of diameter, which, under the microscope becomes an optical magnification of 5000 to 20,000,

PLATE I.

120 °/₀

130 °/₀

140 °/₀

(a)

(b)
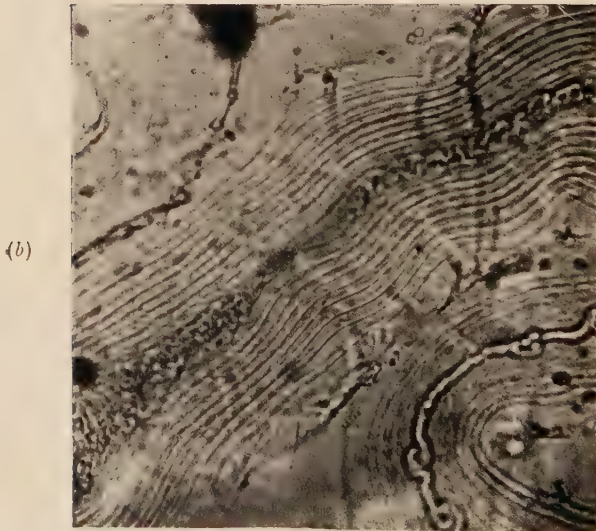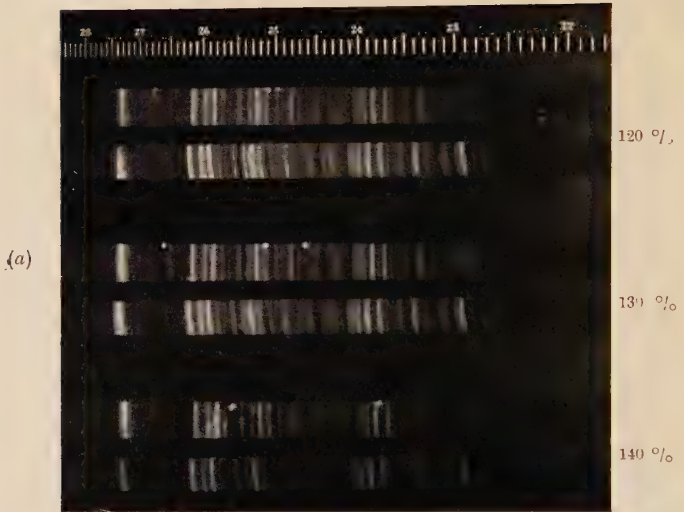
(a) Fluorescent power of bleached linen in terms of that of a cream
wove s.f. paper. —(S. J. Lewis.)   See p. 37.
(b) Cotton fuzz-hairs, thirty-sixth day.—(W. L. Balls.)   See p. 15.

Observation from the lower limit brings to demonstration the important detail of structural differentiation of the cell wall (daily growth rings), shortly described as follows : 'The dimensions of the wall of the lint hair are such that the thickness of each of the twenty-five growth rings comprising it can only be at most about 0.4μ, much less than the wave-length of sodium light.'

The original paper is illustrated by photomicrographs and a diagram of the cotton hair thus built up of concentric layers

0. 100 m. m.
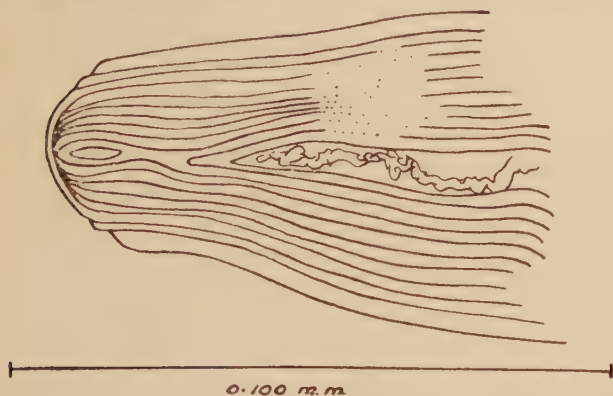
FIG. 1.—Drawing of the tip of a cotton fuzz-hair swollen by hydration treatment, showing growth rings.—(W. L. Balls.)

of substance (cellulose), which constitutes a *resumé* of the very numerous observations which establish this particular feature of differentiated structure (Fig. 1). In Plate I., *b*, is reproduced a photograph of the cotton hair at the thirty-sixth day of growth. The cuticular remains are evident as spirals, and the firmness of the growth layers in the jelly under bending stresses will be seen in the corners. The magnification of the growth rings in this case is 5000. We are indebted to the Royal Society for permission to produce these illustrations. (See also Plates III., IV.)

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It may be pointed out for the further critical appreciation of these researches, that the particular effects of hydration are reversible, and the 'reverted' cotton cellulose is indistinguishable from the original, and consequently the effects in question are a re-hydration of the plant colloid to a condition similar to that which characterises its structural elaboration in growth. Cellulose is an anhydride *qua* constitution ; is elaborated in the condition of a gel-hydrate, dehydrated during maturation to the anhydride form of the complex, which form is persistent and resists reversal by physical actions, and requires specific chemical attack on the reactive groups to determine integral hydration.

In the cases of structural break-down now to be described there are correlative modifications of chemical structure or constitution. Those which are obviously determined by chemical reagents, mainly oxidants (oxycellulose effect) and acids (hydrocellulose effects) are merely mentioned here as the complementary section of the subject of 'cellulose structure,' to be dealt with later in systematic order (Chap. V.).

We are here concerned with structure as such : the organic structures of the plant world, which are either 'cellulose' or derivative complexes. As forms of matter they are colloids, and their properties are those common to this highly diversified group of products. As chemical individuals they are differentiated within the groups, as they are from one another ; as structural individuals shaped by vital processes they present an obvious further differentiation, and it is a purpose of the present discussion to inquire into the correlative effects of this particular origin.

In a general physical inquiry, it is obvious that the relation of cellulose to the active forms of energy, heat, light, electricity, is such as to involve chemical changes under their action, but in relation to mechanical force, it is not obvious that pressure externally applied can produce effects other than change of form, or under extreme action, disintegration of visible structure.

Disintegration of Cellulose Structures by Mechanical Action.—The following special cases have been investigated :—

(*a*) BREAK-DOWN OF COTTON FABRICS UNDER BEETLING TREATMENT.—M. Fort (*J. Soc. Dyers and Col.*, 1918, **34**, 215, also *ibid.*, 1919, **35**, 271).

(*b*) BREAK-DOWN OF COTTON ROPE USED FOR POWER TRANSMISSION.—C. F. Cross (*ibid.*).

(*c*) BREAK-DOWN OF WOOD STRUCTURES (COMPRESSION FAILURE OF AEROPLANE PARTS).—W. Robinson (*Trans. Roy. Soc.*, 1920).

(*d*) BREAK-DOWN OF KAPOK UNDER PRESSURE COMPARED WITH COTTON.—C. F. Cross and H. Stanger.

These cases of structural break-down are noteworthy for the evidences of more fundamental change than the mere loss of cohesion ; and of disintegration under conditions which appear to exclude external chemical reaction.

The total destruction of a web of cloth under the 'beetle' hammering which produces the special 'beetle finish' was accompanied by exceptional features, as observed and described by M. Fort. There was no evidence of antecedent tendering of the fabric by chemical action in the bleaching processes, nor of exceptional treatment which might occur under certain circumstances. The examination of the disintegrated powder of 'cellulose' (Cross and Bevan) showed a profound constitutional change marked by a large conversion to the alkali-soluble form β-cellulose. The microscopical features of the powder, moreover, were quite distinct from those of a shredded fabric, such as is usually formed in processes of mechanical attrition.

*   *   *   *   *   *   *

Attempts to repeat the result have failed. There is no difficulty in devising conditions that will tender a fabric, nor in

developing local tendering, due to excessive heating, with the usual features of the brown of a 'scorched' fabric. But the changes in the cellulose substance as regards formation of alkali-soluble products under such action, even when extreme, are relatively fractional. Experiment and observation since the date of the original publication have confirmed the conclusions that in the special case the destruction was due to mechanical action only, under conditions certainly exceptional and extraordinary, which remain to be discovered and reproduced.

The second case is that of break-down of a cotton rope used for power transmission on the main drive of a cotton spinning mill (Cross). The form of break-down, which arrested attention for its exceptional features, was the conversion of the yarn (untreated, or raw cotton) at the core into rounded hyaline masses, of small dimensions. A critical examination of the specimens warranted the conclusion that the fibrous colloid had been transformed through a phase of hydrate 'fusion' into the structureless form in question, of which the only possible operative causes were of the mechanical-physical order.

Another case investigated is that of changes in woodsubstance (lignocellulose) determined by mechanical stress, such as compression, acting on the wood structures. We note the work under its title—

'THE MICROSCOPICAL FEATURES OF MECHANICAL STRAINS IN TIMBER AND THE BEARING OF THESE ON THE STRUCTURE OF THE CELL-WALL IN PLANTS.'—W. Robinson (*Trans. Roy. Soc.*, 1920 (B), **210**, 49).

The advance made in this valuable contribution is the discovery that the initial phenomenon of the permanent deformation of wood, whether under end-compression, longitudinal tension or shearing, is *the development of microscopic planes of slipping in the substance of the cell-walls of the wood,*

PLATE II.
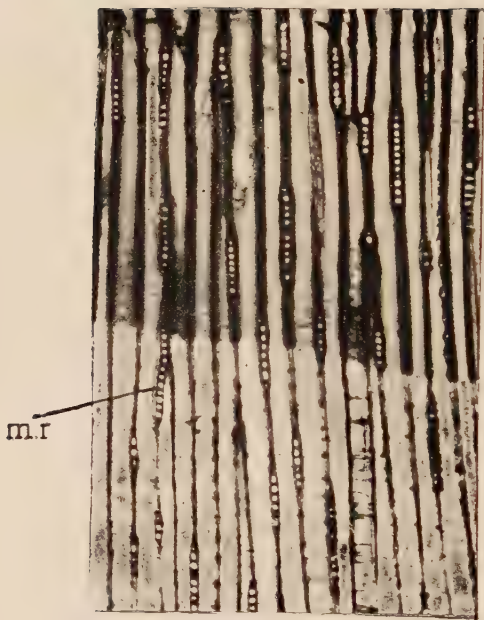
16
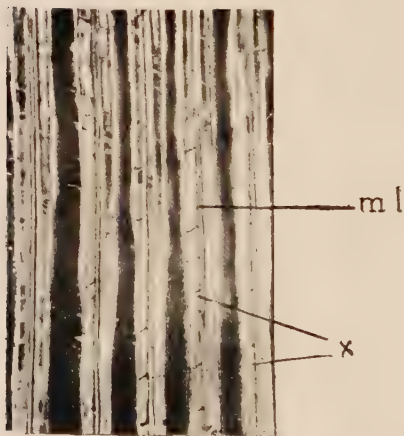
17

Sections through zone of failure of spruce wood. No. 16 stained with chlor-zinc iodide; No. 17, between crossed nicols. *m.r.*, medullary ray; *m.l.*, middle lamella; *x*, slip lines.—(From *Phil. Trans.*, 1920.) See p. 19.

these planes also being more or less definitely orientated in relation to the direction of the stress. While the grosser characters of failure previously described are probably due to the anatomical structure of the wood, yet the appearance of these planes of slipping in the cell-walls in every case precedes them (Plate II.).

The displacement of the particles in the vicinity of the slip-planes causes a remarkable change in the reaction of the wood-substance towards such reagents as chlor-zinc-iodide— a deep blue resulting in this case recalling the colour and characteristic of cellulose. The normal 'lignin' reactions with phloroglucinol, however, can still be obtained (see Plate II., 16, and further, p. 153).

The area in which failure has taken place is thus readily demonstrated, but an even more useful method has been found in that when viewed between crossed nicols the zone of failure stands out as a bright band across the unaltered parts of the section, this band corresponding exactly with the zone brought out by staining methods (Plate II., 17).

Describing the failure of spruce wood under end-compression, the author states that when deformation begins in the cell-walls of the wood, parts of the substance are pushed over other parts so that regular planes of slipping are locally developed. The fact that the lines indicating the boundaries of these planes are sometimes inclined at (approx.) 45° to the axis of the cell, shows that they are probably planes of shearing in the substance of the walls.

As the failure proceeds, the number of planes rapidly increases, with the result that an extended region of the wall is affected until finally the wall buckles or is thrown into a series of crinkles.

The walls thus exhibit plasticity, and it is by this microscopic, plastic deformation of the substance of the cell-walls that the failure is initiated. Whether buckling or crinkling

C 2

subsequently occurs is determined by the relative thickness of
the walls of the tracheides.   The evidences are interpreted by
Robinson as pointing to a displacement of adsorbed lignone
originally in the form of films overlaying the ground cellulose
of the tracheides.

Plate II., No. 16, shows a tangential longitudinal section
through the marginal portion of the zone of failure of spruce ;
No. 17, walls of the tracheides of autumn wood in radial longi-
tudinal sections.   Oblique planes of slipping visible in the
secondary layers, but not in the middle lamella.

*   *   *   *   *   *   *

These observations are all indicative of a plastic property
of cellulose and lignocellulose manifested under conditions
of action of mechanical force.   The cases investigated have
exceptional features, but the effects group themselves with the
transformations of the fibre colloids under the beating treat-
ment of the papermaker.   The operations of milling in contact
with water are designed to produce limited effects : but these
in certain directions may be exaggerated, notably the effects of
'hydration.'

Thus, the 'Jackson Beater,' in which the fibre colloids in
contact with water are exposed to the action of hammers carried
on a central axis, and brought into action by centrifugal lifting
against the sides of the cylindrical container, the colloids are
rapidly hydrated to the 'gel condition.'   In the Arledter
Vacuum Beater these effects of colloid hydration are extremely
rapid.   Since this beater is of the ordinary type as regards
beater-roll and bed-plate, the special effects which it produces
are, in part, to be referred to the removal of the air contained in
the tubular fibre cells, which offers a resistance, obviously great,
but difficult to measure, to the penetration of water through the
actual surfaces of the fibre substances.   This resistance and
the mechanical functions of cellular air contents are illustrated

in the properties of the Kapok fibre about to be described : in regard to papermaking-celluloses and their wet-beating preparation they are brought into very clear evidence by comparison of the effects of beating, under ordinary atmospheric pressure, and under the alternating vacuum pressure conditions of the Arledter beater. The effects generally are highly complex, and although of fundamental importance as the basis of a leading cellulose industry, they have been little investigated otherwise than as mass effects in relation to power consumption.

These considerations open up the subject expressed in general terms as the relationship of plant structures and their components to mechanical force : with the derived problems introduced by concomitant factors of water and oxygen and their interactions, and the auxiliary effect of light, heat, and electrical actions.

KAPOK FIBRE. *Structural Properties.*—During the War period this fibre has come into prominence by reason of its use in marine life-saving appliances which depend upon exceptional properties of structure and composition. A smooth-walled air-filled tube, with a considerable resistance to compression, constitutes a mass which, when tightly packed in a container, occupies 10 to 12 c.c. per gram of substance. This exaggerated specific volume is conditioned by the air contents of the tubes and the interstitial air spaces of the mass under compression. Both offer resistance to wetting by water, and hence the particular technical applications.

As an incident in investigations of relative flotation capacity, various specimens of the fibre have been examined for resistance to extreme compression by R. H. Stanger, and have been compared with cotton. The following data were established :—

(a) Volume of 1 gram under compression by hand.	(b) Load required to reduce (a) to ½ vol.	(c) Break-down pressure.
Kapok . . 10·0 c.c.	3·2 atm.	100 to 120 atm.
Cotton . . 3·62 c.c.	7·5 ,,	720 to 840 ,,

The compression tests were carried out in such a way that the fibre mass was under the compressed air pressure, and the break-down was observed to be a maximum at the centre of the mass.

*   *   *   *   *   *   *

The results are recorded for their purely empirical value, and as indications of a direction of investigation requiring extension in development of the general subject of this section. It would be particularly important to determine the actual loss of volume of the fibre substances : for which, however, it would be necessary to subject them to compression in an inert liquid as medium.

In the sequence of this discussion we have now to notice systematic investigations of specific volumes of cellulose and derivatives carried out in the Laboratory of Messrs. Courtaulds Ltd., and also in association with Dr. S. Judd Lewis, who undertook the more elaborate scheme of continuous observation with progressive rise of temperature : the investigation embracing a number of selected types of cellulose and derivatives.

In the former, observations were confined to ' viscose silk ' and the determinations were made by (a) the displacement method and (b) the ' flotation ' method in mixtures of liquid carbon compounds of the required range of densities.

The results expressed as volume (c.c. per 1 gram) are for series (a) in

Water	0·623	The maximum variations for
Carbon tetrachloride	0·658	the several series of deter-
Xylene	0·654	minations were ± 0·005 from
Heptane	0·657	the mean.

In the (b) series, the following figures were obtained :—

<div style="text-align:center">

Carbon tetrachloride and xylene   0·663

Carbon tetrachloride and heptane   0·669

</div>

As a first conclusion it might be affirmed that the difference in volume estimated in water and in organic liquids, 0·623 —

0·660 = − 0·037, represents loss of volume (5·7 per cent.) due to penetration of the cellulose by the water in 'wetting,' a loss of the same order as that due to mixture of water with alcohols. But wetting is complicated by surface action, and we cannot affirm that 0·66 is the true volume of the cellulose substance, since there may be a compression film of the organic liquid on the surface, with the loss of volume.

Various methods have been devised for measuring the actual volume in air, but the errors are too large for a trustworthy final figure. This is regrettable, as it is especially important to determine the actual volume changes of cellulose in the loss and regain of 'hygroscopic moisture:' such data would give a basis of criticism of the conclusions of physicists as to the actual mechanism of the exchanges with the atmosphere : also would be of particular importance in the control of processes in the cellulose industries. We revert to this question in dealing with particular contributions.

The investigations of S. J. Lewis are in two series, in (A) the temperature intervals of successive observations involved 17 points in the range 20° to 50°, in (B) there were 29 points of observation : i.e. over a large portion of the total duration (6 weeks) the intervals were approximately 1° C.

The records of these investigations are in the form of two reports which describe and discuss in minute detail all the factors of the research which have to be taken into account in arriving at finally accurate results according to the physicists' definition of accuracy.

The publication of these reports (Dec., 1919, and March, 1921) is still reserved pending the elucidation of certain abnormal phenomena : notably the formation of gaseous products. To quote the words of the report : ' The production of large quantities of gas under the conditions of experiment has been fully established : there is evidence that the actions leading to the disengagement of gas occur at temperatures

above 50°. The phenomena not being expected, the opportunity of collecting and analysing the gas was lost. Its removal by the usual methods took considerable time, and it was incidentally observed to be of relatively large amount : it occurred in both series, that is both with water and hydrocarbon.'

The following details of the greater plan of research will explain its scope :—

In both series the selected specimens 14 to 23 grams were contained in glass flasks (200 c.c.) filled with the liquid medium (*a*) water, (*b*) toluene, and heated in a water-filled thermostat of special design : the flasks were kept immersed in the water and removed only at the periodical intervals of observation, the observation being of the usual form of weighing after adjustment of the level of the liquid medium at the particular temperature.

The elaborate range of experimental detail will be appreciated on the general statement that the scheme was designed in clear view of the many sources of error, those incidental to the method, and particularly those introduced by the composition and structural form of ' organic ' fibrous materials, and to establish figures of definite accuracy.

In series (A) the range of selected specimens was as follows :—

1. *Purified Cotton.*—' Purified ' by removal of mechanical impurities, and by treatment with solvents of ' non-cellulose ' components.

2. *Normal Cotton Cellulose.*—Prepared as for ' gun-cotton ' process.

3. *Mercerised Cotton.*—In the form of yarn.

4. *Wood Cellulose.*—Pulp purified by bleaching and extraction with solvents.

5. ' *Viscose Artificial Silk.*'—From wood cellulose.

6. *Cellulose Acetate.*—$C_{12}H_{15}O_5(OAc)_5$; acetone-soluble.
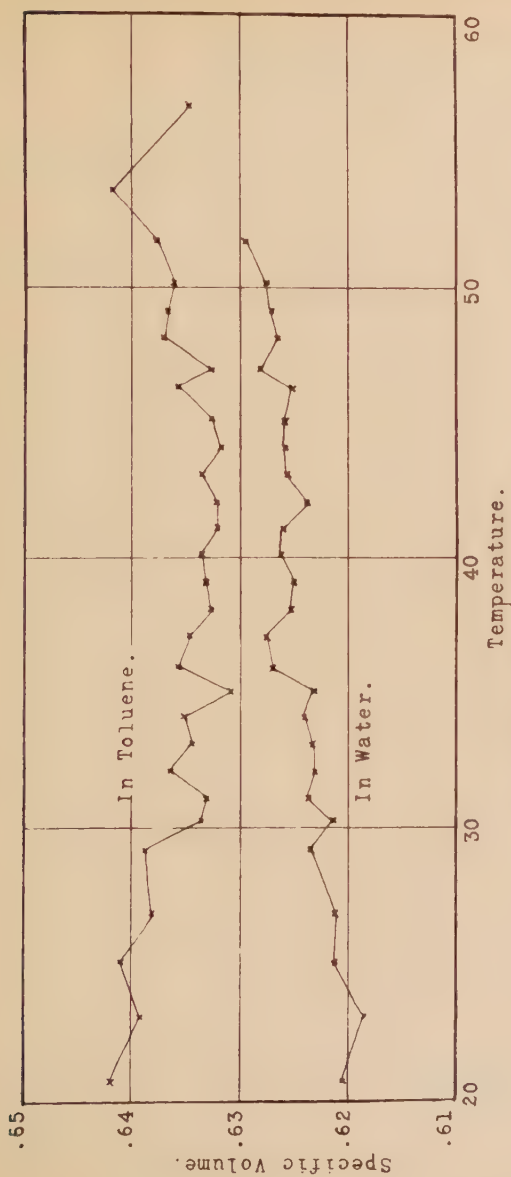
7. *Silk.*—Purified by boiling in soap.

FIG. 2.—Variation in the observed specific volume of cotton cellulose.

In series (B) the specimens were as follows :—

1. *Purified Raw Cotton.*—Egyptian 'sliver' treated with neutral solvent liquids.

2. *Purified Cotton*, i.e. treated with neutral solvents, alkali (Na_2CO_3) boiled and again extracted with solvents.

3. *Normal Cotton*, as in series (A).

4. *Hydrocellulose* } specially prepared.
5. *Oxycellulose*

From the results of the research there are certain conclusions definitely established. Thus, from a survey of the whole of the curves Vol./Temp. of both series, diagrammatic general curves have been drawn emphasising the marked changes of volume in the range 26° to 42°, indicating a correlation with properties of cellulose which determine its physiological functions.

Fig. 2 (on previous page) is selected from the actual curves of experimental results as representative of their general features.

From a comparison of the curves it is noted that in water the apparent volume shows a general increase with rise of temperature, whereas, in toluene there is a corresponding *decrease* up to 45°.

By reason of the phenomena of gas production which are marked in the higher range, 50° to 80°, the observations are subject to an error which remains to be investigated. A critical revision of all the incidents of the phenomena appears to exclude any cause which could be described as accidental. It marks both the observations in water and in toluene : therefore appears to be independent of bacterial action. Moreover, in the water sub-series of series (B), an addition of phenol (0·1 gram per 100 c.c.) was found to be without influence. The weight statistics of the experiments were carefully reviewed : the original weights of the specimens, and the weight observed at the conclusion, established a general loss of substance : but

the data are complicated by notable exceptions, of *gain of weight*, and in both series.

The solids soluble in the liquid media at the conclusion of the experiments were fractionally minute in the case of 'normal' specimens : and only marked in the case of oxy-cellulose, hydrocellulose, and purified (raw) cotton, and in conformity with observed losses of weight of the specimens. This state of matters is noted intentionally to explain the reservation of full publication of these researches : and to point out that it involves the critical separation of an anomaly, which may be an index of an undiscovered property or relationship, from a mere error, of the order of an illusion or unreality.[1]

So far, the review of evidence excludes the latter : the reality of the anomaly is the problem still under investigation.

Reverting to the consideration of the actual data established, some major points to be noted are :—

(1) Oxycellulose is characteristically divergent : the initial apparent volumes in water (*a*) and toluene (*b*) are nearly equal : the final divergence at 55° reaches 0·628/0·645. In each series (A) and (B) moreover, the oxycellulose diverges from the other four types. We shall deal with the bearings of these observations under the section Oxycellulose.

(2) Hydrocellulose, takes a mean position and is the least variable in volume, the range being in water 0·620-0·625, and in toluene 0·630 and 0·637, i.e. about 1 per cent.

(3) Cotton cellulose, in the three forms as described, shows the following ranges :—

	(*a*) In Water	(*b*) In Toluene
Purified (raw cotton)	0·613-0·626	0·643-0·647
Purified cotton	0·623-0·628	0·631-0·642
Normal cotton	0·623-0·628	0·632-0·642

[1] Huebner has recently found (*J. S. Chem. Ind.*, 1922) that when cellulose is treated with water at 35° C. for a few hours, an aldehyde is produced which can be separated by distillation.

These ranges all lie between 1 and 2 per cent. The mean variations, as between the volumes in water and in toluene lie between 2-4 per cent. It is to be noted that the volumes in toluene are uniformly higher than in water.

The general characteristics of the curves establish : (1) The alternations of volume throughout the range of temperatures under which observed. (2) Increase of volume with temperatures in the case of water : decrease in the case of the hydrocarbon.

At this stage of the investigation these general features are rather to be insisted upon than any final figure, or figures purporting to represent the actual volumes.

Such final figures for mean volume of cotton cellulose are—

In water, 0·623 ; in toluene, 0·639.

But the mere difference of these, approximating to 3 per cent., is sufficient to show that we are still dealing with a complicating factor, the interaction of solid substance with liquid medium, with consequent change of volume and the difficulty of allocating the change of volume. From the investigations of physicists in this field, it would appear that the interaction of solid and liquid at the delimiting surface is marked by compression of the contact film of liquid to such degree that an apparent volume of solid—determined by the displacement method—in evaluation to the true volume requires correction to 20-30 per cent. in terms of the compressibility of the liquid medium in which observed.

A particular research (A. M. Williams, ' Forces in Surface Films') involving such procedure is noted below as typical, and presenting a point of view to be taken into account by S. J. Lewis in bringing his researches to their final form. On the other hand, the chemistry of the fibre-colloids and our previous researches on cellulose and derivatives anticipate some of the phenomena of volume variations now more definitely established.

The reactions of hydration or rehydration of these colloids through all the stages, from the absorption of 'hygroscopic moisture' to the formation of plastic hydrate-gels, must be attended by penetration of the colloid system by water, as a molecular effect. In the earliest stages the combination with water produces profound modifications of the mechanical-physical properties of the solids, out of all proportion to the effects of a mere dilution of colloid substance by 10 per cent. (more or less) of water.

For the distinctive chemical relationships of 'hygroscopic moisture' the evidences have been dealt with in previous volumes, and we need only refer to Will's elaborate research, 'Hygroskopizität von Nitrozellulose' (1904, *Mitt*, Neu-Babelsberg), to emphasise this as a generally accepted conclusion. On this view the general differences in apparent volume in water and in hydrocarbon, is due to loss of volume by water in penetrating the colloid, and, in fact, linking up with the OH groups of the ultimate constituent molecules, with a probable loss also of the carbohydrate complex under rearrangement of constituent groups. But this does not exclude an interaction of the hydrocarbon and the colloid, of the same order, if of relatively small magnitude. This is indeed inferentially suggested by the research previously noted, in which higher figures for apparent volumes were obtained in the case of carbon tetrachloride (0·660) and heptane (0·67) ; indicating a lesser degree of penetration than in the case of the aromatic hydrocarbons.

There are further points of evidence in S. J. Lewis's researches for this view of the cause of loss of volume.

A comparison of the curves for cellulose acetate in water, and in toluene, shows a maximum difference of only 0·006 in the earlier phases (28° to 29°) ; equal volumes at 40°, from this point the inverse relation, and again equality at 59°. This is specifically antagonistic to the view of surface film compression

of the liquid medium, as the cause of loss of volume.   In this instance, in fact, no loss of apparent volume can be affirmed.

Another case is significant.   It is clear that wood cellulose, transformed to 'artificial silk,' must undergo a large reduction of 'surface' in the sense of the present discussion, also, that silk as a cylinder of colloid matter is characterised by minimum surface in relation to natural cellulose fibre of similar dimensions. A comparison of these bodies in regard to volume (S. J. Lewis, Series (A)) shows no characteristics of divergence such as should be caused by a multiple extension of surface.

Having prepared the reader for a more critical consideration we now give a condensed abstract of the paper in question.

FORCES IN SURFACE FILMS.

A. M. WILLIAMS (Proc. Roy. Soc., 1920 (A), **98**, 223).

In determining specific volumes of solids by the method of displacement of a liquid medium, it may be assumed that there is a surface film of a gram liquid per 1 gram of solid of mean sp. vol. V_2, the liquid in bulk having the sp. vol. V_1. The sp. vol. of the solid being V, as against V_0, the calculated volume, then

$$V = V_0 + a(V_1 - V_2) \qquad . \qquad . \qquad . \quad (1)$$

with solids of large surface a is large and with compressible liquids $(V_1 - V_2)$ also.

A second series of variations of V_0 is due to variation of surface actually accessible to different liquids.

Thus the above expression holding for water, the expression for chloroform would take the form—

$$V + aV' = V'_0 + a'(V'_1 - V'_2) \qquad . \qquad . \quad (2)$$

Assuming equal penetration power of a series of liquids and that a can be determined by adsorption from the vapour phase, equation (1) becomes

$$V = V_0 + a \cdot p V_1 \beta$$

equation (2) takes the form

$$V + aV = V_0 + a \cdot p V_1 \beta$$

where p is the pressure changing V_1 to V_2, and β the mean compressibility of the liquid. The author identifies this compression force with those which condition cohesion in liquids and represented by a/V_2 in Van der Waal's equation—

$$(p + a/V_2)(V - b) = RT$$

and after discussion of the conditions of the interfacial film, it is finally assumed that the whole fluid in the adsorption area is of sp. vol. V_2 under an attractive force $a_0^{\frac{1}{2}}/V \times a^{\frac{1}{2}}/V_2$, functioning both as an external and 'internal' pressure, the film being as if under an external force p such that

$$p + a/V_2^2 = a_0^{\frac{1}{2}}V \times a^{\frac{1}{2}}V_2$$

In the next section V_0 is determined for a selected and purified specimen of blood charcoal immersed in (a) water, and (b) chloroform, and the mean values obtained at $25°$ C. were (a) 0.511 and (b) 0.461.

The values of a determined by adsorption of vapour were (a) 0.75 grm, (b) 1.26 grm. $= 0.85$ c.c., which lead to the calculations—

$$V = 0.511 + 0.75(1 - V_2/V_1)$$
$$= 0.461 + 0.85(1 - V_2^1/V_1^1)$$

whence

$$0.85 V_2^1/V_1^1 - 0.75 V_2/V_1 = 0.5$$

In regard to the direct object of the investigation these data lead to an evaluation of the sp. vol. of the charcoal

$$\text{from (a) } 0.51 + 0.16 \Big\} 0.67$$
$$\text{,, (b) } 0.46 + 0.21 \Big\}$$

Incidentally the mathematical treatment of the data on the lines of the *a priori* discussion leads to the conclusion that the attractive pressure in the surface film on the charcoal is of the

order of 10,000 atmospheres, and the internal pressure of the charcoal itself is of the order of 50,000 atmospheres.

These data are also applied to the discussion of the potential differences and apparent charge on particles, especially colloids, in suspension in liquid media.

Postulating Planck's formula for the effect of pressure on chemical reactions in solution—

$$\frac{d \cdot \log K}{d \cdot p} = \frac{V_1 - V_2}{RT}$$

applied to reactions of the type

$$R' + OH' + H' + X' = R' + X' + H_2O$$

and taking for $V_1 - V_2$ the data of change of volume on neutralising a strong base by a strong acid in dilute solution ($+ 18$ to 22 c.c. for molar volumes) the author deduces the relation $10^{-5}/10^{-7}$ for the concentration of the $H'OH'$ in the adsorption layer and free liquid medium in the case of water.

Lastly, applying Nernst's formula for diffusion P.D. in solutions of ionic concentration C_1, C_2 the final result is a calculated $E = -0.034$ volt, i.e. in the particular case the charcoal particle immersed in water will appear with a negative charge of this order.

* * * * * * *

We have reproduced the substance of this contribution as illustrating a method of treatment of these phenomena which must be kept in prominence by chemists while following lines of reasoning which develop from a different original conception.

The obvious criticism is that the experimental basis is slender, the substance selected for its property of ' surface large enough to give the effect sought for,' viz. blood charcoal, is a complex of quite unknown constitution, the difference of volumes observed in water and in chloroform is large (10 per cent.) and of contrary order from those of other observers, notably Cude and Hylatt for charcoal (*J. Amer. Chem. Soc.*, 1920, **4,**

(A), 391), and S. J. Lewis for ' celluloses,' etc., above discussed ; and lastly the ' correction ' of the values determined for volumes by increases of 35 to 45 per cent. on the basis of theoretical treatment involving more than one hypothesis, is not justified *a priori*, nor confirmed by observations in air, the probable error of which would be a fraction of the above increases.

In view of the Courtauld and S. J. Lewis researches, and results, the authors' results and conclusions cannot be accepted : on the other hand, the theoretical treatment of the subject matter is valuable and suggestive, and must be taken into account in the still deferred full treatment of the more elaborate investigation of the celluloses and derivatives.

As has often been insisted upon, these present a controlled variation of constitution and properties, which specially qualify them as a basis of investigation of colloids generally, and more particularly the borderland chemical-physical phenomena, such as surface actions, which characterise these forms of matter.

In concluding this section we have to notice researches on the relation of cellulose and derivatives to the forms of dynamic energy—light, heat and electricity.

Fluorescence.—The fluorescent property of cellulose, first observed by W. W. Hartley (*J. Chem. Soc.*, 1893, **63**, 245), has been studied by S. J. Lewis, with the view of establishing a definitely methodical basis of comparison of the effects.

The following is a short account of his results communicated as an interim report to the Society of Dyers and Colourists :—

ON THE FLUORESCENCE OF CELLULOSE AND ITS DERIVATIVES.

S. J. Lewis (J. Soc. Dyers and Col., 1921, **37**, 201).

The main facts and issues of the earlier part of this research were described in a paper published in this *Journal* (1918, **34,**

167). The paper was of a preliminary character, and in referring to the prospect of further work it drew attention—

(1) To the difference in procedure from that of Hartley, namely, that Hartley adopted a method by ' reflection,' while the new work described was by ' transmission.'

(2) To the difficulty of attaining results of any reliable quantitative value.

(3) To the problem of correlating papers or fabrics of the same material, but of varied thickness.

These and some other matters presented themselves for discussion, and put questions which demanded definite answers if anything satisfactory was to be accomplished.

The method of so-called ' transmission ' described in the paper cited leaves nothing to be desired from the qualitative standpoint. The method was devised in an attempt to utilise the apparatus available ; but nothing can be more striking than to find that, under the conditions of experiment, the photographic film remains unaffected until a piece of paper or fabric is placed between it and the source of light. It is complete proof of an alteration in the wave-length suffered by the incident light.

The so-called ' transmission ' method, the nature of which has been considered (l.c.), appears to be inadequate when it is required to take account of, or correct for, the effect of the thickness of the material, as already described (l.c.), and when some truly quantitative measure of the fluorescent power of the material is the object in view. The mechanical hindrance of the light, both incident and degraded, by the opaque, or comparatively opaque, fibres is a sufficient explanation of the difficulty to be overcome.

It is perhaps unnecessary to give details of the many abortive attempts to discover a means to the end in view, first by the ' transmission ' method, which yielded no truly satisfactory results, and then later by gradually elaborating the method

of ' reflection,' which proved, it is believed, in every way efficient.

In the former report (l.c.) Hartley's method of observation was described. His optical arrangements were of the simplest type, and not suitable for critical study ; in particular they were certainly not adapted to a photographic investigation of the fluorescence of the material.

The term ' reflection ' (in inverted commas) has been used to describe the phenomena, because the fluorescence has the appearance of being reflected ; but the expression is misleading, first because the fluorescent light is not reflected, secondly because it is very necessary to distinguish these phenomena from those of reflection which they so nearly simulate in appearance.

It is suggested therefore to use the expression fluorescence ' at the surface ' or the like, as free from that confusion.

The method of observation as now used will be described in greater detail in the full report. In principle it is to allow an ultra-violet spectrum to be focused on the specimen of paper or fabric placed in the position usually occupied by a photographic plate in a large quartz spectrograph. This re- sults in a fluorescent glow being emitted from the surface of the material, and this is photographed by means of a special camera of the ordinary type, the lens of which is inserted in the back of the camera of the spectrograph. This arrangement is novel. Since the field covered by the lens is illuminated by ultra-violet light only, and the lens is of glass, which will not transmit ultra-violet light, it follows that the glow photographed consists of visible light which has been produced by the cellulose degrading the incident light. Further evidence of the degradation of the light and of the effect not being due to reflection (proper) is afforded by the variable degree to which the different specimens give the effect, some being quite inactive. No doubt some ultra-violet light is reflected from

the surface of the fibres of the material, but this is filtered out
by the glass lens.

The quantitative values have been obtained by times of
exposure, a special wedge for the spectrograph being used for
the purpose. The 'fluorescent power' of a given specimen is
then recorded in terms of the fluorescent power of a selected
specimen taken as a standard.

The well-known principle of ordinary and spectro-photo-
metry was adopted, that the eye, either by direct observation
or through the medium of the photographic negative, can
determine equality or inequality, but not the degree of in-
equality. Hence, following the practice of spectro-photometry,
a series of pairs of simultaneous photographs was taken, the
one member of the pair, the specimen under investigation,
being always the same, the other member being the standard
photograph differing each time by the time of exposure.

For example, supposing for the specimen in question ten
photographs of the fluorescent glow to be taken, and numbered
1 to 10, the exposure in every case being one hundred minutes,
also ten similar photographs for the standard, but the exposures
to be respectively 100, 90, 80, 70, 60, 50, 40, 30, 20, 10
minutes.

Then assuming the specimen to be less powerfully fluor-
escent than the standard, it will be found that at some wave-
length the intensity of the two members of the pair will be
equal when the exposure for the standard is 90 minutes. It
follows that if the specimen required 100 minutes to produce
the same effect as the standard produces in 90 minutes, the
specimen has a fluorescent power which is 90 per cent. that
of the standard.

Similarly, at some other wave-length, the two photographs
will match when the standard was exposed for 80 minutes and
so on, indicating that the fluorescent power is 80 per cent.

In this way every region of the spectrum may be explored

to any desired degree, and the results tabulated and graphically represented by a curve, plotting the fluorescent powers as ordinates and the wave-lengths as abscissæ.

It has been found that materials differ very much as to their power of degrading the ultra-violet light. This is exemplified in the case of two specimens as shown in the table and in the photograph (Plate I., *a*) and curve (Fig. 3) accompanying this report. They display the fluorescent power of bleached linen in comparison with that of a sample of cream wove paper, satin finish, 19 lb. to the ream, taken as a standard.

The experimental figures (which have not yet been properly corrected) are as follows ; they serve to show the general character of the work. The wave-lengths refer to the incident light and not to the fluorescent light produced.

Wave-lengths.								Fluorescent power of the bleached linen in terms of that of the standard.
2250	.	.	.	.	.	.	.	500 per cent. probably.
2340	.	.	.	.	.	.	.	180 ,,
2360	.	.	.	.	.	.	.	147 ,,
2380, 2560	.	.	.	.	.	.	.	140 ,,
2470, 2520, 2660	.	.	.	.	.	.	130 ,,
2495, 2510, 2675	.	.	.	.	.	.	120 ,,
2740	.	.	.	.	.	.	.	110 ,,
2840	.	.	.	.	.	.	.	100 ,,
2935	.	.	.	.	.	.	.	90 ,,

The photograph shows three pairs of bands, the upper member in each case being that from the standard, and the lower that from the linen. The white dots mark the points where the two bands are of equal intensity ; the first being the 120 per cent., the second the 130 per cent., and the bottom one the 140 per cent.

The intensity and definition of the bands in the photograph show the degree of success attained with the process of recording the fluorescent glow.

The table and the curve show clearly that two materials may differ not only in the magnitude of their fluorescent power in general, but they show also what is of greater interest, that they may vary greatly in their relative powers in the different
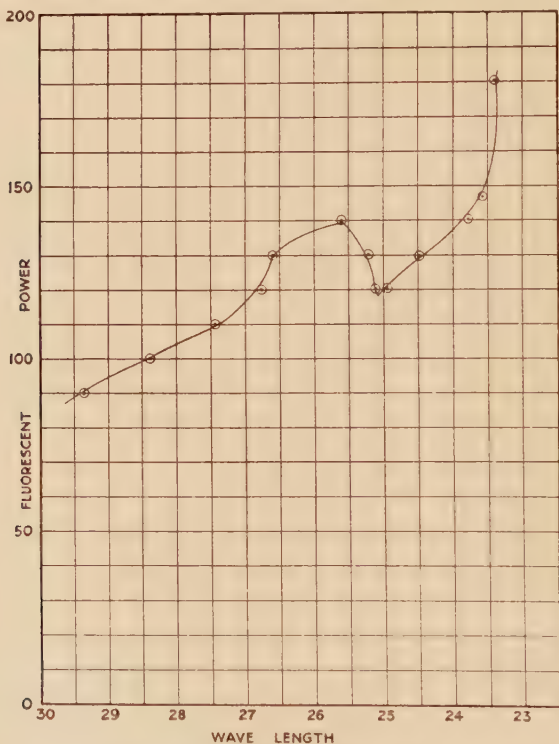

Fig. 3.—Curve exhibiting the fluorescent power of bleached linen in terms per cent. of the fluorescent power of a sample of cream wove s.f. paper.

regions of the spectrum. If the two specimens did not differ in this respect, but differed only in fluorescent power for all regions of the spectrum equally, the curve would take the form of a horizontal straight line.

Among the specimens examined so far are the following : various grades of linen, various filter papers, bank paper, sliver, viscose films, starch paste and gelatin.

The following special series of specimens is now in preparation by Mr. Cross : a normal paper, and the same acetylated, nitrated and parchmentised.

These will all be described individually in the full report. In general it may be remarked that a 'band' such as that shown between wave-lengths 2520 and 2680 in the accompanying curve is not common, but the investigation has not gone far enough to say whether this is a general phenomenon or not ; it is one which requires special and thorough study to justify generalisation.

It is a matter of considerable importance to decide on some material to be used as a standard.

At first the "cream wove" paper with which the linen was compared was used, and with it several comparisons were made with a view to settling on some paper which might be expected to be of uniform quality from time to time. Filter papers offered the greatest promise on account of their reputed constancy of character and composition. A sample of Whatman's No. 30 gave the best results, and a new supply was obtained. This proved altogether different in its fluorescent power, although possibly not different in the character of its fluorescence.

The makers recommended Whatman's No. 44 as the most reliable for constancy, and this turned out to be more satisfactory than any other, especially in being strongly fluorescent in light of smaller wave-length. Indeed this specimen gives very uniform results in all regions of the spectrum, and was adopted as the new standard.

The search for a standard thus led to some interesting results, more particularly in showing that papers which are undoubtedly constant in the ordinary sense are by no means constant in fluorescent properties.

These differences in fluorescence may be only the expression of some accidental state or condition, but if so its nature is not evident. Trials were made with portions of the same paper, one air-dry and the other thoroughly damp, when the damp proved only a little less active than the dry. Similarly other attempts were made to compare portions of the same paper air-dry and immediately after drying at 100° without discovering any marked difference. Hence there appears to be no reason for doing other than employing the specimens in the ordinary air-dry condition.

Although the variation among specimens of the same type is so great and so marked, it is not so great as that obtaining between, say, a normal cellulose and its more fluorescent acetyl derivative on the one hand, or between the normal cellulose and its less fluorescent nitroderivative on the other.

It is well known that the cellulose complex is in a labile state, and it may be that the chemical groups which make up the molecule or molecules which build up the architecture of the physical unit become rearranged or orientated variously under slight alterations in the manufacture of the paper, so that at one time an arrangement tending to simulate the acetyl derivative prevails, while at another time an arrangement resembling that obtaining in the nitroderivative is dominant.

Such hypotheses are mere speculation at the moment, but they gain support from such observations as the following :—

(*a*) Other cuttings from the same piece of the strongly fluorescent bleached linen described above, which had been stored for several months in another place in the same room, apparently under similar conditions, proved less fluorescent.

(*b*) Starch granules are strongly fluorescent, but dried starch jelly made from the same starch is not fluorescent at all.

All this signifies that much of the future research must be directed to working with specimens the nature of which is

thoroughly well known; for example, such as those named in the following summary.

The research hitherto has elaborated methods of experiment both qualitative and quantitative, and discovered the general fluorescent properties of cellulose and its derivatives, showing that specimens differ not only in their fluorescent power but also in their selective properties for light of various wave-lengths. It has demonstrated quite clearly that materials taken for the same by the manufacturer and the expert are by no means the same from the standpoint of their fluorescent properties.

Thus two No. 30 Whatman filter papers taken from different batches were widely different. Nevertheless, repeated experiments show that the same specimen gives approximately constant results from time to time.

The further investigations are to elaborate the foregoing details as may seem desirable, but especially to do quantitative work on specimens of known character. For example, to obtain two or more specimens of each, (*a*) pure cotton paper, (*b*) pure linen paper, (*c*) pure esparto paper, (*d*) pure cotton fabric, (*e*) pure linen fabric, (*f*) pure silk fabric, (*g*) pure wool fabric, (*h*) cellulose acetate of as nearly as possible known constitution in the form of paper, fabric, film, (*i*) others, and arrive at some conclusive results as to the differences which correspond with known differences of constitution or character, working out a few varieties thoroughly rather than attempting to explore a wide field.

This presumes the preparation of special specimens, the need for which could not be recognised until recent work had demonstrated the variability of specimens reputed to be the same.

* * * * * * *

As to constitutional changes determined by the action of light —some researches dealing with the action of ultra-voilet light

are described fully in Chap. V, pp. 119, 123. As will be seen the results show that the rays have a specifically destructive action on cellulose when air is excluded as perfectly as possible (Gaede pump), or when the exposure is made in an atmosphere of hydrogen.

In the presence of oxygen the effect is to convert the cellulose into 'oxycellulose,' due no doubt to the action of the rays tending to the production of ozone.

The relation of cellulose to electrical energy does not seem to have been studied beyond the point to which it was taken in the preliminary work of Cross and Bevan (*J Chem. Soc.*, 1895, **67,** 433), continued later by Darling (*Electro-Chemist*, 1904, **3,** 566).

The relation of cellulose to heat energy receives attention in the following important paper :—

A THERMAL STUDY OF THE CARBONISATION PROCESS.

H. HOLLINGS and J. W. COBB (J. Chem. Soc., 1915, **107,** 1106).

This research was designed to follow the phases of the process of destructive distillation of coal in regard to endothermic and exothermic character : incidentally to deal with the problem of absorption or evolution of heat, occurring in a mass of coal at a comparatively low temperature, as affecting the liability to spontaneous heating under storage : lastly, the basis of investigation was widened to include cellulose, 'dehydrated cellulose,' and lignite, regarded as the first and earlier stages of the series of natural products characterised by progressive accumulation or concentration of carbon.

The specimens investigated in the last section were as follows : cotton cellulose approximately normal ; 'dehydrated cellulose' made by the action of H_2SO_4 on cotton cellulose—solution in acid followed by heating at 70° C. (Cross and Bevan, *B.A. Report*, 1881, 603 ; *Phil. Mag.*, 1882 (v), **17**, 327) and purifying the colloidal black condensation product ; lignite—the Bovey-Tracy variety.

The following are the details of elementary composition of the specimens :—

		C	H	O	S	N
Ash °/₀						
—	Cellulose	44·4	6·2	49·4	—	—
1·13	Dehydrated cellulose	58·1	4·1	36·7	1·1	—
5·20	Lignite	63·0	6·3	28·7	1·7	0·5

Per cent. ash free substance.

The 'dehydrated cellulose' and lignite each gave 65 per cent. 'volatile matter' determined by heating in platinum crucible (method of *Amer. Chem. Soc.*, 1899). The S in 'dehydrated cellulose' must represent residual combined (SO_4H) groups.

The method is based upon observations of temperature of the substance heated comparatively with a similar mass of a standard substance (coke), which may be presumed to be thermally inert. In the curves plotted in Fig. 4, the deflections to the left represent the negative or endothermic phase ; those to the right a plus of temperature (increase) by comparison with the rise of temperature of the standard.

With cellulose the evolution of heat is very sudden at 345°, due apparently to chemical action. In the case of dehydrated cellulose and lignite the evolution is spread over a wider range (280° to 420°) ; with coal it does not begin below 400°.

The results, discussed in relation to probable errors, warrant the general conclusion that these substances, under the action

of heat, pass through a succession of alternating phases of absorption and liberation of heat energy.

*   *   *   *   *   *   *

This research has no obvious connection with those involving the study of changes comprised within the range of temperature 20° to 120° C., for the results are obtained with the cellulose, or other substances, under progressive decompositions of complex character, involving condensation and resolution ; therefore changes of configuration and volume.

No.1 Lignite   No.2. Dehydrated cellulose   No.3 Cellulose.
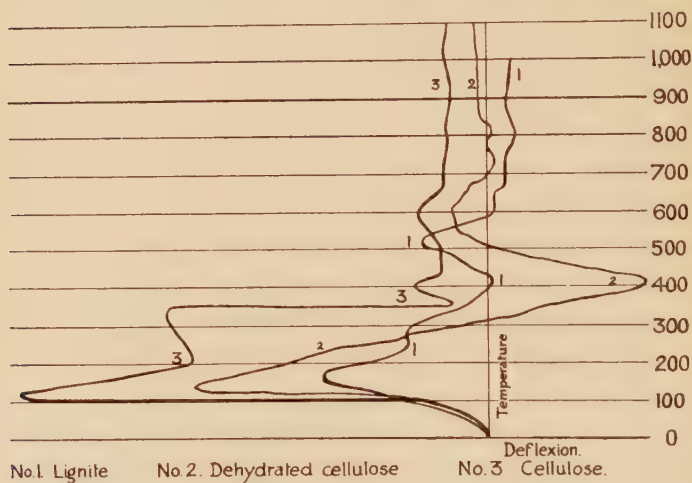
FIG. 4.

But the observations of S. J. Lewis on volume changes with temperature, indicate phenomena of a similar order, the volume changes having the alternating character, with many incidental evidences of a variable heat capacity in relation to the temperature conditions and effects.

Exact results in this region are not yet obtainable, and it is only necessary to direct critical attention to the problem of determining the heat capacity or specific heat of cellulose, to

bring into prominence the exceptional experimental difficulty involved. For the present we must be content with the generalised conception of a highly mobile aggregate affected constitutionally by heat exchanges.

Solutions of Cellulose.—We have in previous volumes dealt with the solution of cellulose as a general question on the type of the zinc chloride solution, regarding this as a reciprocal interaction of acidic and basic groupings both in the cellulose and in the solvent. The solution of cellulose in cuprammonium would appear to involve the more specific properties (or functions) of carbonyl groups. W. H. Gibson (*J. Chem. Soc.*, 1920, **117**, 479) has carried out a very careful investigation on these solutions with the object of standardising a cellulose raw material for ester (gun-cotton) formation. He has shown that the condition of the original can be diagnosed in terms of the viscosity of a solution in a cuprammonium of definite preparation and condition. The results obtained are valuable (see p. 215), but the explanation of the interesting phenomena observed is not attempted. We therefore mention the following paper by Hess in which the phenomenon of optical rotation of cellulose in cuprammonium solutions is confirmed and discussed :—

THE ASYMMETRIC STRUCTURE OF CELLULOSE.

K. Hess and E. Messmer (Ber., 1921, **54** (B), 834).

The authors in preliminary observations confirmed the results of Levallois (1885) that ammoniacal copper hydroxide solution (Schweizer's Reagent) is optically inactive.

Solutions of cellulose in the reagent are optically active, two determinations giving $[a]$ $-950°$ and $-1000°$ respectively. On the other hand, solutions of 'regenerated' cellulose in HClAq are inactive as are also solutions of ethylcellulose in

ether, cellulose xanthogenate in aqueous alkali, and cellulose jellies in neutral salt solutions. The authors regard cellulose therefore as a striking example of 'latent asymmetry' resembling mannitol, the cuprammonium solution apparently behaving in relation to cellulose as boric acid does in the case of some carbohydrates. On the 'celluxose' theory of Hess (p. 82), the explanation is given that the copper atom diverts the secondary valencies which hold together the celluxose groups in cellulose, forming an ammoniacal copper celluxose complex to which the observed optical activity is due. Some evidence for this was given by the observation that the specific rotation of sucrose in cuprammonium solution diminishes as the proportion of copper increases, to zero value when there are three molecules of sucrose to five of copper, increasing subsequently.

*   *   *   *   *   *   *

The facts above must be accepted and the observation of asymmetry made to fit in with future views of the cellulose complex.

Isolated observations have capriciously revealed many new solvents for cellulose, but it now appears from recent work that the formation or non-formation of solutions of cellulose is capable of generalised expression, and we accordingly notice two researches in which such general views are formulated, one by P. P. von Weimarn (1912) and the other by H. W. Williams (1921). The latter we reproduce in full, partly owing to its publication being in a journal not perhaps readily accessible, but more especially for its qualities of precision and concise exposition which make it a model for the student of this section :—

THE DISPERSOID CHEMISTRY OF CELLULOSE.

P. P. von Weimarn (Z. Chem. Ind. Kolloide, 1912, **11**, 41).

The author has already given a general theory of the peptisation process for the production of dispersoid (colloidal) solutions (*Grundzüge der Dispersoidchemie*, 1911). In extension of this he shows that cellulose can be converted either into a plastic condition, or into a colloidal solution by treatment with aqueous salt solutions. Certain conditions of concentration, pressure, temperature and time of action have to be maintained, these varying with the nature of the salt. To carry out the peptisation of cellulose 3 grams are suspended in 100 c.c of water, the salt (lithium chloride, calcium bromide, manganese thiocyanate, etc.) is added and heat applied. After a sufficient effect has been attained the solution is either cooled or diluted, and the gelatinous cellulose separated.

To obtain a dispersoid (colloidal) solution the heating and addition of the salt are continued until peptisation is complete ; from the colloidal solution hydrated cellulose can be recovered in different forms by means of various coagulating agents. The products thus prepared, on account of their high degree of dispersion, are very reactive. With some salts, e.g. iodides of sodium, strontium and calcium, bromide of calcium, thiocyanates of calcium, strontium and barium, the process can be carried out at atmospheric pressure ; with others, such as sodium, potassium and barium chlorides, increased pressure is necessary. With concentrated sodium chloride solution peptisation begins at 170° C. under 8 atm. pressure. To prevent decomposition of the cellulose it is preferable to increase the pressure so as to work at a moderate temperature. With saturated solutions (at boiling temperature and atmospheric pressure) peptisation proceeds rapidly with the nitrate and halogen salts of lithium, the iodides of sodium, calcium and

strontium, and the thiocyanates of calcium, strontium, barium and manganese.

Solutions containing 1 per cent. of cellulose set to transparent jellies on cooling, and if these are exposed to air the salts effloresce, leaving a skeleton jelly of hydrated cellulose. With other salts which peptise only on prolonged heating, decomposition of the cellulose to substances of lower molecular weight takes place. Cellulose swollen by previous soaking in concentrated saline solutions can be peptised much more readily than untreated cellulose. (Compare also Ger. Pat. 275,882 (1912) and H. G. Deming, *J. Amer. Chem. Soc.*, 1911, **33**, 1515.)

THEORY OF THE SOLVENT ACTION OF AQUEOUS SOLUTIONS OF NEUTRAL SALTS ON CELLULOSE.

HERBERT E. WILLIAMS (Manchester Memoirs, 1921, **65**, 12).

The object of this paper is to demonstrate that the solution of cellulose in certain aqueous solutions of neutral salts is largely a physical phenomenon, chemical reaction playing but a small part ; that it is independent of the chemical nature of the salt, but that it depends directly on certain physical properties of the concentrated salt solution, and on the power of the salt to form hydrates in solution.

During a research on the preparation and properties of the metallic thiocyanates and their double salts, it was noticed that the concentrated solutions of several of these salts had a profound action on paper. Several years later attention was again directed to this subject, and a systematic study of the action of the concentrated solutions of the thiocyanates on cellulose was undertaken. A number of pure thiocyanates were prepared, and the action of their concentrated solutions

on cellulose carefully observed, both in the cold and on heating. As the action on cellulose varied a little with the particular form of cellulose used, and the treatment it had undergone, the experiments described in this paper were carried out with chemical wood pulp taken from the same bulk sample ; thus ensuring a cellulose of a uniform condition.

The solvent action of the solution was determined by suspending a small portion of the chemical wood pulp in the solution and allowing the mixture to evaporate by slow boiling. A sample was taken out from time to time and examined on a glass slide under the microscope, and the temperature of the boiling-point of the solution noted when fibre structure was no longer visible and the drop on the slide appeared perfectly uniform and homogeneous. The solution was then diluted and the precipitated cellulose washed and examined for possible evidence of structure. The experiment was then repeated, taking in this case a solution but a few degrees below the boiling-point noted in the first experiment. When the salt solution is obtained of the right concentration for dissolving the cellulose, solution of the cellulose may be obtained in most cases below the boiling-point of the salt solution, but in all cases, in order to obtain complete solution by this method it is necessary to heat the mixture to a minimum temperature varying between 90° to 133° C., depending on the particular salt solution used. With pure neutral calcium thiocyanate solution boiling at 133° C., solution of the chemical wood pulp may be obtained by heating to 90° C.

This work resulted in the discovery that concentrated solutions of the calcium, strontium, magnesium, manganese, and lithium thiocyanate were each solvents for cellulose when heated.

On careful examination of the solutions of those salts which dissolved cellulose, it was noticed that in each case the solution of sufficient concentration to dissolve cellulose was

IV.   E

abnormally viscous, a property shared by zinc chloride solution, which has long been known to be a cellulose solvent.

This idea of a possible relationship between the viscosity of a salt solution and its solvent action on cellulose was submitted to critical examination, and the viscosities of the solutions of a number of thiocyanates were determined at different concentrations, at constant temperature, by means of the Ostwald viscometer.

These results showed that as the concentration increased, the viscosities of the solutions of the calcium, strontium, magnesium, manganese, lithium, and aluminium thiocyanates rapidly increased, whereas the solutions of the potassium, sodium, ammonium, nickel, and zinc thiocyanates increased but slowly ; the former group being much more viscous than the latter for equal molecular concentrations.

Now the concentrated solutions of the calcium, strontium, magnesium, manganese, and lithium thiocyanates had been found in the course of this work to be solvents for cellulose, but no solution of the cellulose was obtained with the aluminium thiocyanate solution, although the viscosity of its concentrated solution was high. With the thiocyanate solutions of low viscosity such as those of potassium, sodium, etc., no solution of the cellulose was obtained at any concentration. With the one exception then of the aluminium salt, the high viscosity very sharply differentiates those aqueous solutions which dissolve cellulose from the non-solvent solutions of low viscosity, and clearly indicates some relationship between a high viscosity of the salt solution and the property of dissolving cellulose.

A further examination of these cellulose solvents revealed the fact that not one of them dissolved the cellulose until the boiling-point of the concentrated solution rose to 133° to 134° C. or over. This fact is strikingly shown by the solutions of the strontium and manganese thiocyanate, which are more

viscous than the calcium salt at the concentration at which the latter dissolves cellulose, yet neither of these salt solutions becomes a cellulose solvent until concentrated to the boiling-point of 133° C. This point would seem to explain the non-solvent action of the aluminium thiocyanate solution, the most concentrated solution of which did not boil above 121° C. under atmospheric pressure.

At this stage a very large number of the solutions of the thiocyanates and double thiocyanates were examined, and the viscosity of the solutions at various concentrations determined. Calcium chloride, a very soluble salt and one with a viscous solution, was also examined in this manner. The figures thus obtained were then plotted against the corresponding boiling-points of the solutions.

As no solution of these salts was so far known which dissolved cellulose under a concentration corresponding with a boiling-point of 133° C., this figure was taken as the minimum boiling-point of a solution for a cellulose solvent ; and also as not one of these solutions, even those boiling above 133° C., was a cellulose solvent unless the solution had a viscosity at 100° C. of at least 3·3 times that of water at 20° C., these two points were taken as the lower limits of these properties in the solvent action of these solutions on cellulose. On these facts it was temporarily assumed that before an aqueous salt solution could dissolve cellulose, it must have a boiling-point of 133° C. or over, and a viscosity at 100° C. of 3·3 times that of water at 20° C.

In Fig. 5 the reason for fixing these two lower limits is very clearly shown, particularly by the lithium, strontium, barium-manganese, $BaMn[CNS]_4$, and cerous thiocyanate, for the last three of these have a much greater viscosity than calcium thiocyanate of cellulose solvent strength, yet they do not become solvents unless concentrated until the boiling-point of the solutions rises to 133° C. On the other hand, lithium

thiocyanate solution does not attain the necessary viscosity until the boiling-point rises to 165° C., at which concentration it becomes a cellulose solvent.

With the exception of the solutions of calcium chloride, and potassium-manganese thiocyanate, $K_2Mn[CNS]_4$, all these solutions were found to be cellulose solvents at the particular

A Lithium Thiocy: G Calcium Chloride
B Potassium   "   H Pot: Mang: Thiocy:
C Sodium   "   J Strontium   "
D Calcium   "   K Manganese   "
E Magnesium   "   L Barium Mang: "
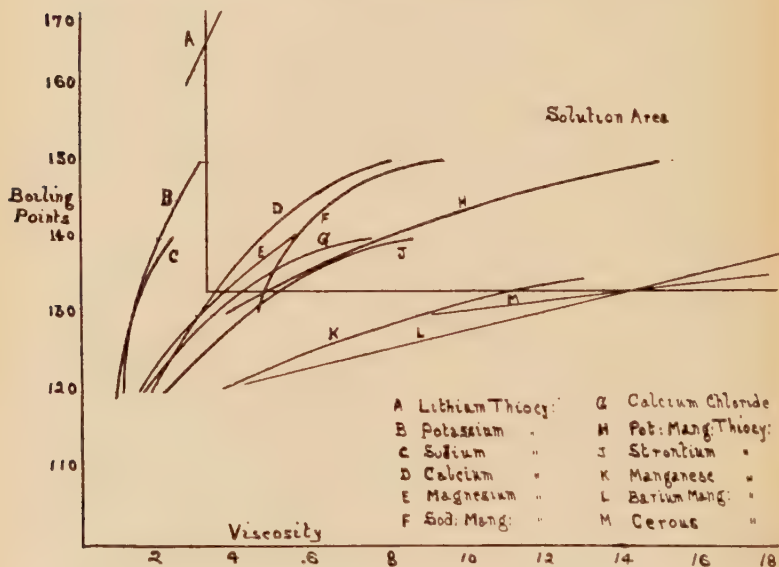F Sod: Mang: "   M Cerous   "

Fig. 5.

boiling-point concentration and viscosity at which the curve crosses into the area marked 'cellulose solvent area.'

The two exceptions mentioned above were at first difficult to explain, and it was realised that there was at least another factor to be brought to light before the necessary physical constants for a cellulose solvent could be established.

A consideration of this question suggested the following line of reasoning. If one of the necessary preliminary conditions before the cellulose dissolves is the hydration of the cellulose, it is evident that if the water present in the aqueous solution is attached to the salt with too great an affinity, it will not hydrate the cellulose, but on the contrary will tend to dehydrate it ; and no solution of the cellulose can result, although the concentration and viscosity conditions are fulfilled.

In order to test this point the heat of dilution of these aqueous salt solutions was determined at different concentrations, and the molecular heat of dilution plotted against the boiling-points. These determinations were not of high accuracy owing to the difficulties of such operations in a works laboratory ; but the results obtained were sufficient to give the necessary explanation. It may be of interest here to remark that early in this work it was found that to dilute the solutions of the different salts with the same quantity of water, as in the usual practice, gave results that were without definite meaning. On gradually diluting many of these concentrated solutions an evolution of heat is at first observed up to a point ; further dilution beyond that point results in an absorption of heat. With concentrated calcium thiocyanate solution heat is evolved on gradual dilution until the molecular ratio of salt and water is 1 : 20 ; further dilution beyond this point results in an absorption of heat. With strontium thiocyanate solution this point is reached at the ratio of 1 : 18 ; and calcium chloride solution at about 1 : 30. In order to obtain the true molecular heat of dilution it is necessary first to determine this ratio for the particular salt under observation, and to determine the heat evolved by diluting the concentrated solution to this point.

The results obtained in this manner showed that the concentrated calcium chloride solution has a very high heat of dilution, much higher than that of any of the other salts examined ; whereas the potassium-manganese thiocyanate

solution has a large negative heat of dilution. The former solution therefore at this concentration would have too strong a dehydrating action to dissolve cellulose, but the
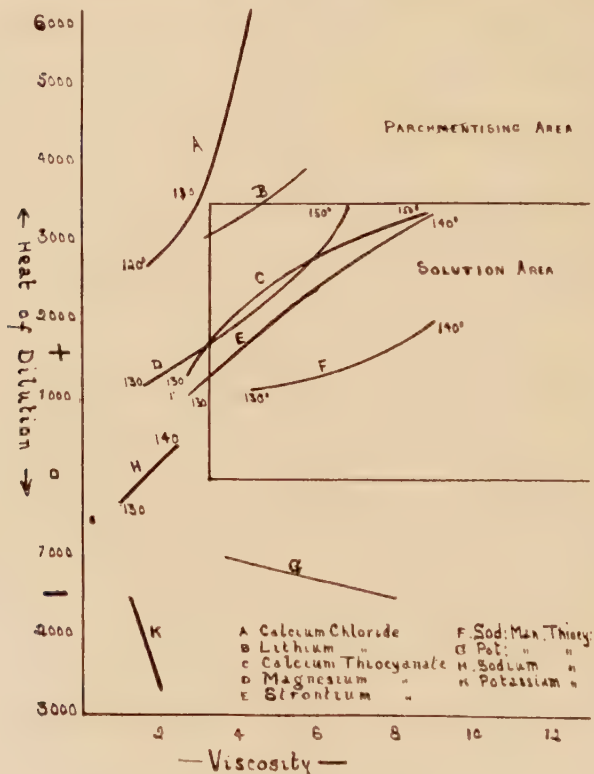

FIG. 6.

latter would have neither a dehydrating nor a hydrating action.

As calcium chloride with so large a heat of dilution was a non-solvent for cellulose, it was thought possible that if the

calcium thiocyanate solution could be made concentrated enough, a point should be reached when its heat of dilution would be so great that it would cease to be a cellulose solvent. Experimental evidence showed this to be true for a solution concentrated to a boiling-point of 150° C. and over. At this concentration no cellulose was dissolved even after heating for some time, though the fibres appeared highly swollen. The addition of a very small amount of water, sufficient to drop the boiling-point of the solution to 148° C., caused the cellulose to dissolve rapidly.

In a similar manner strontium thiocyanate solution of boiling-point 140° C. and upwards proved to be a non-solvent for cellulose, and magnesium thiocyanate solution of boiling-point 150° C. and above. Slight dilution to reduce the boiling-point below these figures caused almost instantaneous solution of the cellulose.

From these facts it appears evident that we could plot out the molecular heats of dilution against the viscosities of the solutions for various concentrations, and mark off a sharply defined area ; so that any aqueous solution of a salt of boiling-point 133° C. or over, the molecular heat of dilution and viscosity of which fell within the prescribed area, would be a solvent for cellulose, and not otherwise. And further it would begin to dissolve cellulose, at all concentrations corresponding with boiling-points above 133° C. on the viscosity and heat of dilution curve within this area, and cease to be a solvent where the curve passed out and beyond that area.

This area could of course be very clearly defined on a three-dimensional scale model, marking the viscosity, heat of dilution, and boiling-points of the solutions on the three axes.

It will be noticed on examining the curves given in Fig. 6 that whereas potassium-manganese thiocyanate is well out of the solvent area owing to its negative heat of dilution, the

corresponding sodium double salt enters the area. Experimentally all efforts to dissolve cellulose in the potassium-manganese thiocyanate solution of any concentration have failed, but it readily dissolves in the solution of the sodium salt boiling at 134° C.

This difference between the sodium and potassium thio-

FIG. 7.

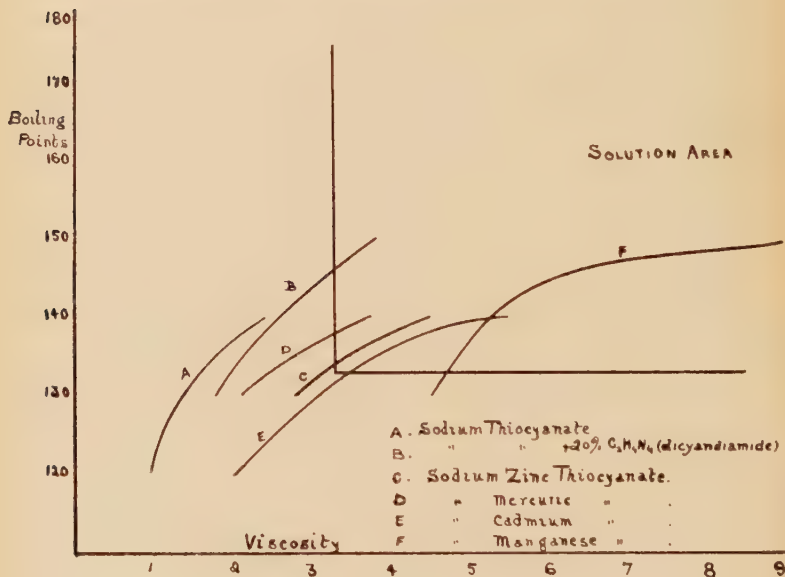cyanates and their double salts is very clearly shown in Fig. 7. The negative heat of dilution of the potassium thiocyanate solution becomes larger and larger as the concentration increases, but with the solution of the sodium salt it becomes less and less negative, and finally positive.

The solution of the sodium thiocyanate fails to become a cellulose solvent because of its low viscosity, and likewise the

potassium salt for the same reason, and also on account of its negative heat of dilution.

The addition of other salts that will either not effect, or will increase the heat of dilution, and at the same time increase its viscosity, should convert the solution of the sodium salt into a cellulose solvent. In Fig. 7 the viscosities and boiling-points are plotted of the sodium thiocyanate solution to which has been added other thiocyanates and compounds, and it will be noticed that in all cases the addition has increased the viscosity of the sodium salt solution, and the curve passes into the area marked 'cellulose solvent area.' All these solutions represented by the curves that cross into the 'solution area' are cellulose solvents, and moreover they only become solvents when the concentration of the solution rises to the point where the viscosity boiling-point curve crosses the 'solution area' and above. A very large number of such additions can be made to the concentrated sodium thiocyanate solution besides those given in the figure, such, for example, as aluminium, chromium, or ferrous thiocyanate, or by dissolving silver, lead, calcium, or cuprous thiocyanate in the solution. All these additions increase the viscosity of the solution, and at the same time convert the sodium thiocyanate solution into a cellulose solvent.

Additions to the potassium salt solutions to increase its viscosity do not, however, produce cellulose solvents, though higher boiling-points and viscosity results ; for all these mixtures so far examined have, unlike the corresponding sodium thiocyanate, a large negative heat of dilution.

Again, lithium thiocyanate solution does not become a solvent for cellulose until concentrated to a boiling-point of 165° C., the viscosity being too low for all concentrations below this boiling-point. If the conclusions arrived at above are correct, it should be possible to lower the concentration at which the solution becomes a cellulose solvent by additions,

which, while not diminishing its heat of dilution, will yet at the same time increase its viscosity. This may be accomplished by a variety of substances, such as other thiocyanates of characteristic viscous solutions as, for example, the manganese, calcium or aluminium thiocyanate. The addition,

A Lithium Thiocyanate
B   "   "   + 10% (NH₄)₂CS
C   "   "   + 20% H₄C₂N₄ *
D   "   Manganese Thiocyanate.
E   "   Mercuric   "
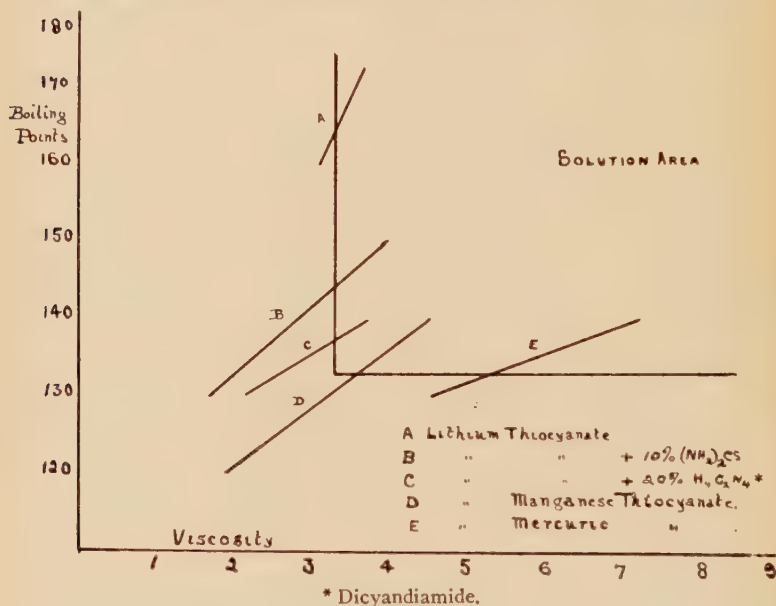
* Dicyandiamide.

Fig. 8.

however, need not be a thiocyanate for thiourea, hexamethylenetramine, or dicyandiamide may be added with like effect. These results are illustrated by curves given in Fig. 8.

It is interesting to note that each of these solutions becomes a cellulose solvent at the particular concentration represented by the point where the boiling-point viscosity curve cuts into the solution area. Lithium thiocyanate solution does not dissolve cellulose until it is concentrated to a boiling-point

of 165° C.; but when the viscosity of the solution is increased by additions of other soluble compounds, a cellulose solvent may be obtained boiling 30° C. lower. Each of these solutions has a positive heat of dilution when concentrated.

It is thus seen that whatever the explanation may be, there is a definite connection between the boiling-point, the viscosity and the heat of dilution of a solution of a neutral salt, and its solvent power for cellulose. This relationship has been very strikingly demonstrated in the course of this work on the thiocyanates, for every thiocyanate either singly, or in conjunction with one or more other thiocyanate solution, has been converted into a cellulose solvent, although the components of these mixtures may not of themselves dissolve cellulose. In each case, however, it has been necessary to bring the viscosity, heat of dilution, and boiling-point within the limits stated above, either by concentrating the solution, or by additions of other thiocyanates either soluble or insoluble—the latter being soluble in the concentrated solutions of the soluble thiocyanates.

These facts apply not only to the thiocyanates, but to all other soluble salts, a number of which has been examined in this manner. Both calcium chloride and magnesium chloride solution when concentrated to the required viscosity have too great a heat of dilution to dissolve cellulose. Additions, therefore, which lower the heat of dilution, and either increase or do not lower the viscosity, should convert these solutions into cellulose solvents. This may be accomplished by dissolving mercuric chloride in these solutions, to form the double calcium mercuric chloride, and the magnesium mercuric chloride respectively. By this means the viscosity is increased and the heat of dilution greatly reduced, and the concentrated solution of either of these two double salts dissolves cellulose.

It may here be remarked that the figures given above refer only to neutral solutions, but if the solutions are made acid by a weak acid such as acetic acid, the cellulose is more readily

dissolved, and in much greater amounts. If, however, the solution is made alkaline, no solution of the cellulose takes place ; for example, if the solution of the calcium thiocyanate is made basic with a little calcium hydroxide, or the strontium salt solution with strontium hydroxide, the solvent action on the cellulose is entirely arrested ; this is true for all the thiocyanates, and probably also for all salt solutions.

The concentrated so'ution of the calcium thiocyanate, which has been more deeply studied than the other salts, not only dissolves cellulose but also dissolves acetyl-cellulose, natural silk, and gelatine ; but has no action on wool. The hydroxides of calcium, lead, zinc, cadmium, cobalt, nickel, ferric iron, and stannic tin are all soluble in the concentrated solution. Both the stannic and the ferric hydroxides only begin to dissolve when the thiocyanate solution is concentrated until the composition of the solution corresponds with the liquid hydrate $Ca(CNS)_2 10H_2O$. This is the lowest concentration that will dissolve cellulose. The curves representing the percentage of these hydroxides dissolved in the cold for different concentrations of the calcium thiocyanate solution show that they all take a sharp upward bend from the point where the composition of the solution corresponds approximately to the formula $Ca(CNS)_2 10H_2O$.

That these hydroxides pass into colloidal solution is shown by the colour of the ferric hydroxide solution which is deep brown, showing no trace of the red colour of ferric thiocyanate. All these hydroxides are completely precipitated on dilution.

It is an interesting fact that ferric hydroxide while soluble in the calcium, strontium, and magnesium thiocyanate solutions, all of which are cellulose solvents, is insoluble in the potassium thiocyanate, and calcium chloride solutions of any concentration, both the latter solutions being also non-solvents for cellulose.

Lead sulphate and tricalcium phosphate are also soluble

to a limited extent in the concentrated solution, while certain water-soluble salts, such as sodium chloride and potassium chromate, are insoluble. In the light of the above facts, it is evident that one of the main conditions of a cellulose solvent is, that not only must the salt combine with water to form a definite hydrate in solution, but that the solution must be so concentrated that it is capable of combining with more water ; the solution therefore, at least in the cold, must consist of a liquid hydrate.

As an aqueous salt solution having the necessary viscosity and boiling-point, but which is not hydrated or only partially hydrated in solution, and therefore contains free water, is a non-solvent for cellulose, it is evident that the combined water plays an important part in the solution of the cellulose, the solution being brought about by means of the combined water, or the capacity of the salt for taking up water. The combination of the salt and water must, however, be of a certain order, that is to say the water must be bound to the salt between the limits of a maximum and minimum intensity, above or below which no solution of the cellulose can take place on heating.

A simple and possible explanation of the solvent action on cellulose of these salt solutions, which fulfils the prescribed conditions, may be stated thus : The hydroxyl groups of the cellulose unit link up with the salt complex in place of the water molecules, acting in the manner of a substituted water group, thus causing the fibre to swell considerably. The cellulose unit is brought by this means into molecular range with the water molecules combined with the salt. By raising the temperature the union between the salt and water molecules will weaken and tend to part from the parent molecule. The water thus freed migrates to the cellulose by which it is imbibed, causing further swelling of the fibre, which increases as the progressive hydration proceeds. The highly swollen

fibre in the gelatinou condition then peptises, and passes into colloidal solution.

The temperature of the solution would in the first place tend to weaken the union of the cellulose aggregate, and in the second place tend to dissociate the salt hydrate complex.

The minimum temperature of the boiling-point of the solution is probably not a direct function of the solvent action, but, as it has been shown above that in the liquid hydrate required the water must be bound to the salt between the limits of a maximum and mimimum intensity, it is probable that the latter would occur at the same boiling-point with various solutes.

The explanation of the mechanism of the entrance of the cellulose into the salt hydrate complex, by means of its hydroxyl groups taking the place of the water, has some other facts to support it. Thus ethyl-ether, which may be considered as water in which two hydrogen atoms are replaced by two ethyl groups, is practically insoluble in water, and in calcium thiocyanate solution up to a concentration of sp. gr. $1\cdot36$, which corresponds with the hydrate $Ca(CNS)_2 10H_2O$, but dissolves in increasing quantities in the cold solution of greater concentration. With a solution of sp. gr. $1\cdot4$ corresponding to the hydrate $Ca(CNS)_2 8H_2O$ nearly an equal volume of ether is dissolved, and moreover it is a remarkable fact that the amount of ether dissolved is equivalent to the water lost from the decahydrate, molecule for molecule. The amount dissolved corresponds to the formula

$$Ca(CNS)_2 8H_2O 2(C_2H_5)_2O.$$

Conclusion.—The solution of cellulose in an aqueous solution of a neutral salt is independent of the chemical nature of the salt, but is largely dependent upon the physical properties of the salt solution. For such a solution to dissolve cellulose it must consist of a liquid hydrate—an associated molecular

complex of salt and water. But this complex must be of such an order that it has a viscosity above a certain minimum, and a positive heat of dilution between well-defined limits.

These limiting conditions will vary according to the nature of the cellulose, and the treatment which it has previously undergone; but for any particular cellulose the limits will be constant for all salt solutions in water.

RÖNTGEN-SPECTROGRAPHIC INVESTIGATION OF CELLULOSE.

R. O. Herzog (Cellulose Chem., 1921, **2**, 101).

(From J. Soc. Chem. Ind., 1921, **40**, 342A, and 1922, **41**, 8A).

Cellulose fibres in parallel arrangement show a Röntgen diagram similar to that of crystal particles arranged along one axis, and certain conclusions relative to the constitution of cellulose may be drawn from the analogy. From the value of the elementary parallelopiped it would appear that the group $(C_6H_{10}O_5)_4$ is regularly repeated. Further, it is most probable that the symmetry of the rhombic crystal system is represented in the cellulose molecule, although that of the monoclinic system, one degree lower than the rhombic, is not excluded. The fundamental units must each contain a cellobiose residue, and the whole cellulose molecule must be built up of cellobiose groups. Three types of structure come into consideration: (*a*) Open chains of dextrose residues linked together in groups of four in series by means of oxygen bonds. (*b*) Closed rings of four dextrose components linked by oxygen bonds; if the symmetry is that of the rhombic system this possibility is ruled out. (*c*) Cellulose may consist of internal anhydrides of cellobiose; according to the rhombic symmetry the constituent elements would be composed of dextrose

residues in pairs linked by oxygen bonds through the second and sixth carbon atoms. Cellulose, hydrocellulose and viscose exhibit crystal structure, whereas nitro-, acetyl-, and ethyl-celluloses, are amorphous. It is possible, however, to re-establish arrangement effects by stretching and similar mechanical treatment whereby the tenacity is increased and the swelling capacity is correspondingly decreased.

CHAPTER III

SYSTEMATIC CHEMISTRY—CONSTITUTION

THE solution of the problem of cellulose constitution has taken its place as a definite objective of the systematic science, and since the researches towards this end are based upon rigorous quantitative method, the results are important accumulations of data which must be accepted as exact. There are several methods, or lines of attack, with the common aim of resolving the cellulose into bioses, or monoses, or their ester-ether derivatives, quantitatively estimating these, and from the yields and constitution (configuration) deducing an integral constitutional formula for the parent complex.

The characteristic features of these several methods are as follows, cotton cellulose being generally adopted as the typical cellulose and parent substance :—

(1) Solution of the cellulose in ' mineral acids,'

$H_2SO_4 \ldots H_2SO_4 . 2\frac{1}{2}H_2O$, HCl, Aq (41-42 per cent. HCl) dilution with water, and boiling to complete the hydrolysis.

(2) Solution in acetic anhydride, in presence of sulphuric acid : acetolysis to cellobiose octacetate.

(3) Conversion to methyl- and ethyl-ethers by interaction of alkali-cellulose and sulphuric esters and resolution of these.

(4) Distillation under reduced pressure yielding lævo-glucosan.

The results obtained under these several sections are by no means uniform or uniformly interpreted ; this conflict of results, or interpretation, is in itself a progressive criticism, elucidating

the terms of ultimate common agreement ; and we therefore
postpone our own critical comments to follow the brief notice
of the more important researches in this section, merely pre-
mising the point of general criticism of the introduction
(p. 4), and noting that outside any question of interpretation
the following very definite stages of progress have been
achieved :—

(*a*) The recognition of cellobiose as the cellulose sugar ; the
proof of its constitution and its relationship to maltose.

(*b*) The recognition of lævoglucosan as a definite cleavage
product : a carbohydrate of C_6 dimensions produced in large
proportion to the original (50 per cent.), and by a process
which, although technically described as destructive, is not
severe as regards constitutional change. Constitution prob-
ably settled.

(*c*) Preparation of methyl derivatives and their resolution,
particularly, to a crystalline trimethyl glucose of known con-
stitution.

The forward movement resulting in these achievements
may be said to date from the following contribution :—

THE SACCHARIFICATION OF CELLULOSE.

Ost and Wilkening (Chem. Zeit., 1910, **34,** 461).

The conversion of cellulose into dextrose by the action of
dilute sulphuric acid at such high temperatures as 170° to
180° C. has been previously described, but the authors state
that a quantitative yield is not likely to be obtained consider-
ing the sensitiveness of dextrose to acids at such temperatures.
This takes the form, on the one hand, of reversion to iso-
maltose, and, on the other, of resolution to various organic
acids. In proof of this a series of trials was carried out in

which a 5 per cent. solution of dextrose was heated with 2 per cent. sulphuric acid at temperatures ranging from 120° to 145° C. The dextrose remaining was estimated both by the polarimeter and by the copper reduction method. These methods, it is interesting to note, yielded identical results, but the proportions of dextrose surviving the acid hydrolysis varied from 91 to as little as 35 per cent. of the original amount taken.

The authors find, however, that Flechsig's claim to have converted 98 per cent. of the cellulose into dextrose by his modified process is justified. They carried out a series of experiments, the results of which are recorded in a table. One of the best results was obtained by the following procedure :—

Five grams of cellulose were dissolved in 50 c.c. of 72 per cent. sulphuric acid, and after standing three hours the solution was diluted to a content of 3 per cent. of sulphuric acid and 0·25 per cent. cellulose products, and finally digested in the autoclave for two hours at 110° C.

The method of copper reduction gave dextrose equivalent to 100·4 per cent. on the cellulose.

There were also present as a result of hydrolysis, organic acids which gave soluble barium salts equal to 4·3 per cent. (calculated as H_2SO_4) on the cellulose. The specific rotary power of these was $a_D = 44·8°$, and 1 gram of the solid gave 1·15 grams of dextrosazone. Theoretically, 100 of cellulose should give 111 of dextrose. In the table the yields obtained (by copper reduction) are given on this basis when the concentration of the acid, the time of standing, the extent of dilution, and the temperature and time of digestion under pressure, were varied. The yields were always over 100, and in two cases as much as 113·5 and 112 respectively. It is obvious, therefore, that the copper reduction method gives values in excess of the truth. Estimations of the dextrose by yeast fermentation gave dextrose equal to 80 to 83 per cent. of these values in each case.

THE HYDROLYSIS OF CELLULOSE.

R. Willstätter and L. Zechmeister (Ber., 1913, **46**, 2401).

The authors treat cotton cellulose with HClAq of maximum concentration up to 42 per cent. The cellulose dissolves to a viscous solution. After standing, dilution and boiling, the solution is neutralised, and the aldehydic sugars estimated in terms of optical rotation and cupric reducing power upon the results of which the authors claim a quantitative resolution of cellulose to dextrose.

*   *   *   *   *   *   *

Ost, in a later paper (*Ber.*, 1913, **46**, 2995), criticises the above work of Willstatter and Zechmeister in that novelty is claimed for a production of dextrose (estimated by polarimeter) of the order of 90 to 95 per cent. of the theoretical quantity, by a reference to the paper of Ost and Wilkening of 1910.

We may add that the claims for the quantitative production of dextrose by hydrolysis with 42 per cent. hydrochloric acid are not accepted. It is interesting to note that the solution of cellulose in acid of this concentration is described in the textbooks of 1870 (W. A. Miller, 'Organic Chemistry,' 4th ed., 1869, p. 130).

HYDROLYSIS AND ACETOLYSIS OF CELLULOSE.

H. Ost (Annalen, 1913, **398**, 313).

Discussing the question of the relationship of hydrocellulose to cellulose, the author states that while the action of dilute sulphuric acid readily gives hydrocellulose, not more than half the cellulose can be completely hydrolysed to dextrose in this

way, further, that in the progress of hydrolysis from hydrocellulose
to dextrose, no intermediate products are obtained.

Elementary analysis of carefully prepared samples of cellulose and hydrocellulose dehydrated at 120° show no difference in analytical composition. The proportion of water combining in this first stage of hydrolysis, therefore, must be within the limits of analytical error. It is shown that if *dried* at 100° to 105° C. cellulose can then be *dehyarated* at 125° C., and hydrocellulose at 120° C., without decomposition.

Hydrolysed with concentrated sulphuric acid, cellulose forms acid esters of cellulose dextrins. After dilution and heating at 120° C. an almost quantitative yield of dextrose is obtained.

An acid of 70 per cent. strength is, however, a better reagent for the sulpholysis of cellulose.

Cellulose when acetylated in the presence of sulphuric acid as catalyst, gives a series of cellulose-dextrin acetates ending in cellobiose octa-acetate, with a progressive diminution in the viscosity of the solutions. A greater proportion of combined acetyl is found in these products than in cellulose tri-acetate itself. The most favourable conditions for a complete acetolysis to dextrose acetates were found to be: Cellulose one part, mixture of equal weights of glacial acetic acid and acetic anhydride containing 10 grams of sulphuric acid per 100 c.c. of mixture, 11 parts. Digestion at 18° to 20° C. for four to six months. Some cellobiose crystallises out. After pouring into water, the dried precipitate and the water are extracted with ether giving dextrose pentacetate, of which a further quantity can be obtained from the accompanying syrups by acetolysis with mixtures containing a minimum of sulphuric acid.

The part insoluble in ether contains cellobiose acetate, and the intermediate dextrin acetates. On solution in 70 per cent. alcohol the former crystallises, and from the mother liquors the dextrin acetates can be precipitated by water.

Cellobiose and dextrin acetates in the crystalline form have actually been isolated in a yield of 60·6 per cent. of the theoretical quantity. Counting the above dextrin acetates, soluble in ether though not of a crystalline character, the total yield of simple products amounts to 92 per cent. of the theoretical, and the author concludes that the cellulose complex is entirely composed of dextrose residues.

A REINVESTIGATION OF THE CELLULOSE DEXTROSE RELATIONSHIP.

MARY CUNNINGHAM (J. Chem. Soc., 1918, **113**, 173-181).

The conclusion of Willstätter and Zechmeister (*Ber.*, 1913, **46**, 2401) that cellulose on treatment with fuming hydrochloric acid is quantitatively resolved into dextrose, is based on the specific rotation of the end product according to the formula $c = a \times 100/[a]_D$, where $[a]_D$ is the specific rotation of dextrose in 40 per cent. hydrochloric acid. In the present investigation these experiments were repeated, using (*a*) a cotton and (*b*) an esparto cellulose, which is characterised by a high furfuroid content (about 12 per cent. of furfuraldehyde), and would be expected to give end products quite different from those obtained from cotton. The progressive hydrolysis of these with 40 per cent. hydrochloric acid was followed by the polarimeter over twenty-four hours, the curves obtained running parallel and showing a gradual decrease to a value of (*a*) $+ 45·6°$ and (*b*) $+ 41·1°$ respectively. A 5 per cent. solution of the cellulose was used and before the reading was taken the solution was diluted to an acid concentration of 8 per cent. in which, as Willstätter has shown, the specific rotation of dextrose is practically normal.

A similar series of observations was made using sulphuric acid dihydrate (73 per cent. concentration of H_2SO_4). An examination of the products of hydrolysis showed that the celluloses had in every case been converted into polysaccharose esters which were isolated as barium or lead salts. In the case of esparto these compounds bear sufficient relation to the original complex to give a high, but diminished, yield of furfuraldehyde on distillation, but they are distinguished from the cotton cellulose sulphates prepared by Stern (*J. Chem. Soc.*, 1895, **67,** 74) in having a smaller content of inorganic material. In the esparto products the percentage of barium combined is approximately equal to that of the SO_4H, so that the two are present in the ratio of $Ba_2 : (SO_4H)_3$.

This means that if either neutral or acid sulphates, or both, are formed with alcoholic hydroxyl groups, then an excess of barium is present which must be in union with hydroxyl groups of a sufficiently acid character to decompose barium carbonate, whilst the acid character of these hydroxyl groups is further emphasised by the stability of the compounds towards carbon dioxide, and this establishes them as genuine barium salts. The SO_4 residues are also in very stable union, as complete precipitation can only be effected by boiling with concentrated hydrochloric acid, in the presence of barium chloride, for some hours, and although alkaline hydrolysis with barium hydroxide solution greatly increases the barium content, the SO_4 groups are not entirely removed and it is quite possible that some of them are present in the form of a neutral ester.

The solution of esparto cellulose in sulphuric acid after twenty-four hours was diluted, left with barium carbonate and the ester precipitated by alcohol in the form of a deliquescent white powder, containing Ba, 8·6 ; SO_4, 7·9 ; $C_5H_4O_2$ (furfural), 8·3 per cent. After treatment with cold alcoholic acid for some days an ester quite free from barium was obtained. This showed SO_4, 5·3 ; $C_5H_4O_2$, 6·2 per cent. ; $[a]_D + 41·6$.

With hydrochloric acid similar esters containing chlorine were obtained, e.g. products after twenty-four hours' treatment on analysis gave :—

	Pb	Cl	$C_5H_4O_2$	$[\alpha]_D$
Cotton cellulose	8·2	7·3	1·0	47 to 33°
Esparto cellulose	8·2	8·6	5·6	32 to 25°

It is noteworthy that on the further hydrolysis of these products no dextrose could be obtained.

For the optical rotation of cellulose solutions compare also König and Hühn ('Bestimmung der Zellulose,' Berlin, 1912) and Cross and Bevan (*Eighth Inter. Congr. App. Chem.*, 1912, **13,** 101).

*   *   *   *   *   *   *

The two papers which follow are given mainly in the author's own words :—

THE CONSTITUTION OF THE POLYSACCHARIDES. PART II. THE CONVERSION OF CELLULOSE INTO GLUCOSE.

J. C. IRVINE and C. W. SOUTAR (J. Chem. Soc., 1920, **117,** 1489).

Even if cellulose can be regarded as a chemical individual, in the ordinary sense, the customary methods of solving problems of structure are of little avail in view of the insolubility of the compound, the dubiety attending its molecular magnitude, its behaviour as a colloid, and the probability that a fibrous structure is not chemically homogeneous.   As a result many of the statements which find a place in permanent literature are based on very insecure evidence, and are even contradictory.

A normal cotton cellulose is represented by the formula $(C_6H_{10}O_5)_n$, and ideas as to the molecular structure have been formed largely on the evidence afforded by hydrolysis.   It is

important to note that in this particular case hydrolysis is not so readily effected, and involves the use of somewhat drastic reagents, so that taking into account the unstable nature of the hydrolysis products secondary reactions are inevitable.

Apparently the view which finds most acceptance is that cellulose, like starch, is essentially a polyglucose anhydride, and it may be well to state at once that this conception admits of a double interpretation. The complex may consist of simple units, $C_6H_{10}O_5$ (derived from a hexose by molecular loss of water), polymerised in unknown numbers. On the other hand, n molecules of a hexose may be directly connected together through the elimination of n molecules of water, or, where n is a large factor, of $n - 1$ molecules. In either case, the first point which must be settled is to ascertain beyond doubt if glucose is actually the hexose formed by the hydrolysis of cellulose, and if so, to determine exactly the amount of sugar thus produced.

The inquiry becomes much more definite if it can be shown that within the limits of reasonable experimental error, cellulose can be converted into glucose in terms of the equation—

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_{12}O_6$$
$$100 \quad \xrightarrow{\hspace{2cm}} \quad 111{\cdot}11$$
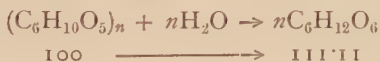
From time to time confident statements appear in the literature that practically quantitative yields of glucose have been obtained from cellulose, but the grounds upon which such claims are made are by no means convincing to workers in the sugar group. Practically speaking, the only experimental methods available for degrading cellulose depend upon the use of mineral acids, either alone or in conjunction with acetic anhydride, and it is evident that any sugar thus liberated must undergo profound alteration when kept in contact with these reagents. This no doubt accounts for the fact that hitherto pure crystalline glucose has never been obtained from this polysaccharide.

Nevertheless, Flechsig (*Zeitsch. physiol. Chem.*, 1883, **7**, 523) claimed that a yield of 95 to 98 per cent. of the theoretical amount of glucose was formed by the action of sulphuric acid on cellulose.

Schwalbe and Schultz (*Ber.*, 1910, **43**, 913) supplemented Flechsig's experiments by isolating the products of hydrolysis, and obtained a semi-crystalline sugar amounting to only 20 per cent. of the theoretical yield. Working on similar lines, Ost and Wilkening (*Chem. Zeit.*, 1910, **34**, 461) made the important claim that the yield of glucose was almost quantitative, but it may be remarked that they examined the products of hydrolysis polarimetrically, and reported specific rotations ranging from $+ 29 \cdot 4°$ to $+ 44 \cdot 8°$, whereas the equilibrium value for glucose is $+ 52 \cdot 5°$.

The use of hydrochloric acid for degrading cellulose is even less satisfactory. As is well known Willstätter and Zechmeister (*Ber.*, 1913, **46**, 2401) dissolved cotton wool in 40 to 41 per cent. aqueous hydrochloric acid, and allowed the hydrolysis to proceed in the cold.

The results appear convincing until they are considered in conjunction with the known effects of hydrochloric acid upon glucose. Willstätter and Zechmeister were of the opinion that owing to the low concentration of sugar in the acid solution, no isomaltose was formed, but it has been shown (Davis, *J. Soc. Dyers and Col.*, 1914, **30**, 249) that the action of hydrochloric acid in promoting the auto-condensation of glucose extends to solutions containing as little as 1 per cent. of the sugar. In addition, few reagents effect more fundamental changes in reducing hexoses than hydrochloric acid in either dilute or concentrated solution. Thus, traces of the acid convert the butylene-oxide forms of glucose into ethylene-oxide isomerides.

That Willstätter's process has very little bearing on the primary constitution of cellulose is further shown (Cunningham, *J. Chem. Soc.*, 1918, **113**, 173) by the fact that both cotton and

esparto celluloses give practically identical rotation curves when hydrolysed with concentrated hydrochloric acid, under the conditions described by him. In fact, the evidence of specific rotation and reducing power, even when apparently consistent, cannot be held to characterise an uncrystallisable syrup as a definite sugar.

A considerable advance on the use of mineral acids, is marked by the conversion of cellulose into glucose acetates as elaborated in the exhaustive researches of Ost and his pupils. Recognisable crystalline products consisting of cellobiose octa-acetates and glucose penta-acetates are thus obtained, so that it is possible to ascribe trustworthy values to the yields. By using acetic anhydride containing, approximately, 10 per cent. of sulphuric acid as the hydrolytic reagent, Ost (*Chem. Zeit.*, 1912, **36**, 1099) isolated a mixture of solid acetates amounting to 60·6 per cent. of the theoretical quantity, the remaining products being uncrystallisable syrups.

It is very doubtful if the latter can be included in calculating the total yield, or if polarimetric methods are admissible in estimating hexose acetates, since many factors combine to render such a method uncertain (Hudson and Parker, *J. Amer. Chem. Soc.*, 1915, **37**, 1589 ; Hudson, *ibid.*, 1591 ; Hudson and Johnson, *ibid.*, 1916, **38**, 1223).

Up to the present time, in no research on the hydrolysis of cellulose, where a yield of glucose even approximating to the theoretical amount has been claimed, have the results been based on the quantity of the sugar or of a characteristic derivative actually isolated. In the work now described, we adhered to the principle that the yield of hexose should be ascertained from the weight of the crystalline compounds, obtained in a condition of analytical purity, and in well-defined stereochemical forms. Adopting this standard, we have been able to show that, as a minimum, the yield of glucose obtained from cellulose is 85 per cent. of the theoretical amount.

The method used by us embodies the same principle as acetolysis in that it involved hydrolysis of cellulose, and simultaneous condensation of the sugar liberated, so as to give a stable derivative which thereafter remained unaffected.

Cellulose was treated as described in the experimental part, with a large excess of acetic anhydride containing acetic and sulphuric acids. When the fibrous structure had disappeared, the product was poured into water,[*] and the precipitated solid separated. The filtrate then contained the lower acetylated glucoses, together with acetosulphates and other soluble degradation products, whilst the insoluble residue consisted of polysaccharide acetates. On heating the latter in an autoclave at 100° with methyl alcohol containing 0·5 per cent. of dry hydrogen chloride, the first effect was to remove the acetyl groups, which were converted into methylacetate (Perkin, *J. Chem. Soc.*, 1905, **87,** 107 ; Fenton and Berry, *Proc. Camb. Phil. Soc.*, 1920, **20,** 1, 16). Thereafter, simultaneous hydrolysis and condensation with the solvent ensued, the process then being parallel with the conversion of starch into methylglucoside (Fischer, *Ber.*, 1895, **28,** 1151). The main product of the reaction consisted of a crystalline methylglucoside ; but about 25 per cent. of the material persisted, and remained practically unaffected on repeating the treatment with acid alcohol. This amorphous residue was therefore hydrolysed by means of dilute aqueous hydrochloric acid, and the product again brought into reaction with acid methyl alcohol. In this way the total yield of methylglucoside from the fraction insoluble in water was ascertained. From this compound there was no difficulty in obtaining pure crystalline glucose.
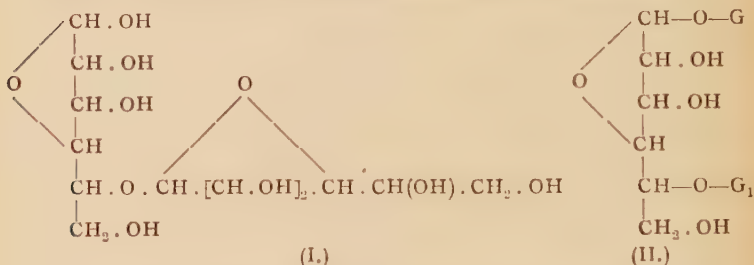
As a rule it is an uncommon experience in the sugar group to obtain crystalline derivatives in yields which exceed 80 per cent., and the figures now submitted thus afford strong evidence that cotton cellulose is composed essentially of glucose residues condensed together. It is to be noted, however, that the

processes adopted by us would not serve to isolate any ketose constituent, should such be present. In view of the fact that cellulose yields bromomethyl-furfuraldehyde (Fenton and Gosling, *J. Chem. Soc.*, 1901, **79,** 361), it is conceivable that the unexplained margin of 15 per cent. may be accounted for by the presence of a nucleus in the cellulose molecule which is resolved into a ketose on hydrolysis. It is possible, though somewhat improbable, that the hexose units in cellulose are symmetrically disposed as in inulin (Irvine and Steele, *J. Chem. Soc.*, 1920, **118**, 1474), and the alternative has to be kept in view that two, three or four hydroxyl groups of individual glucose molecules may be involved in the coupling. Should this be the case, the hydroxyl content of cellulose may still be regarded as three, but this would be an average value and would not imply that, as in inulin, three hydroxyl groups are present in every C_6 unit. Evidence in support of this second view has been contributed by Denham and Woodhouse (*ibid.*, 1917, **111**, 244), from the study of trimethyl cellulose, and we hope in consultation with these workers to extend the investigation on methylated celluloses. Further evidence of the non-uniformity of the glucose linkages in cellulose is afforded by the remarkable variation in the ease with which the component parts of the molecule undergo acid hydrolysis. Another significant factor is that the yield of cellobiose obtained from cellulose, although varying greatly with the conditions of hydrolysis, has never exceeded the maximum quoted by Klein (*Zeitsch. angew. Chem.*, 1912, **25**, 1409). His figures are :—

Cellulose	→	Cellobiose octa-acetate	→	Glucose.
100 parts	gave	60 parts	equivalent to	31·9 parts.

From these results it would appear that at least one-third of the cellulose molecule contains the linkage characteristic of cellobiose. Now, cellobiose contains eight hydroxyl groups, one of which is a reducing group, and therefore terminal. It

follows that one of the remaining hydroxyl groups of the reducing component must be attached to the reducing group of the second glucose residue. The position of this linkage may be fixed from, among other factors, the constitution assigned to trimethyl glucose, and formula (I.) may thus be deduced for cellobiose :—

$$CH.OH$$
$$CH.OH$$
$$O \quad CH.OH \quad O$$
$$CH$$
$$CH.O.CH.[CH.OH]_2.CH.CH(OH).CH_2.OH$$
$$CH_2.OH$$
(I.)

$$CH—O—G$$
$$CH.OH$$
$$O \quad CH.OH$$
$$CH$$
$$CH—O—G_1$$
$$CH_2.OH$$
(II.)

The expanded structure (II.), in which G and G_1 represent glucose residues, can thus be deduced for a fragment of the cellulose complex. Of the two groups G and G_1, the latter is the more stable to hydrolysis, and the system indicated in the formula (II.) evidently represents the most resistant portion of the cellulose molecule. It is significant that in our work we encountered the same progressive difficulty in eliminating the glucose residues from cellulose. The methylglucoside obtained was isolated from three groups of acetolysis products :—

A. Soluble in water.

B. Insoluble in water and hydrolysed by methyl alcohol.

C. Insoluble in water and resistant to acid methyl alcohol.

Our results thus show that the cellulose molecule may be dissected into three portions, and the approximate ratio in which the groups A, B and C are present is displayed below :—

Cellulose 100 parts.	Methylglucoside.		Glucose.		$C_6H_{10}O_5$.
A gave	9·5817	equivalent to	8·9	equivalent to	8·0
B ,,	52·3372	,,	48·6	,,	43·7
C ,,	39·9068	,,	37·0	,,	33·3
			94·5		85·0

It will be seen that the proportion of C agrees approximately with the figure indicated by the maximum yield of cellobiose octa-acetate obtained from cellulose, and it is our intention to continue the investigation by tracing the structural distinction between the units A, B and C. In addition we hope to ascertain whether the glucose belongs to the ethylene-oxide or butylene-oxide types, as the fundamental difference between cellulose and starch may depend on the nature of the oxidic linkage in the constituent hexose residues.

THE HYDROLYSIS OF COTTON CELLULOSE.

G. W. MONIER-WILLIAMS (J. Chem. Soc., 1921, **119**, 803).

The investigations hitherto carried out on the hydrolysis of cellulose have been critically reviewed by Irvine and Soutar (*ibid.*, 1920, **117**, 1489). They point out that up to the date of their work, crystalline glucose had never been obtained in even approximately quantitative yield from the products of hydrolysis, and that conclusions drawn as to the amount of glucose present had invariably been based on the rotation and copper reduction of an uncrystallisable syrup. Irvine and Soutar found that if cellulose was treated with acetic anhydride and sulphuric acid, the mixture of polysaccharide acetates obtained could be converted by heating with methyl alcohol and hydrochloric acid into a crystalline methylglucoside, which gave pure crystalline glucose on hydrolysis. The yield of glucose obtained was 85 per cent. of the theoretical quantity.

The results recorded below are the outcome of an attempt to repeat Ost and Wilkening's work on the direct hydrolysis of cellulose by 72 per cent. sulphuric acid (*Chem. Zeit.*, 1910, **34**,

461). Preliminary experiments, following exactly the method used by these investigators, invariably gave a syrup from which no crystalline glucose could be prepared. Eventually the following procedure was adopted :—

Ten grams of cotton wool were dissolved in 50 c.c. of 72 per cent. sulphuric acid, and the dark-coloured, viscous solution was allowed to remain for one week at room temperature. The cotton wool used contained 6·93 per cent. of moisture, estimated by drying to constant weight in a water-oven at 94°, and 0·13 per cent. of ash. The sulphuric acid solution was diluted to 5 litres with water, and boiled under reflux for a total time of fifteen hours. Traces of volatile fatty acids distilled into the condenser. A slight quantity of a dark-coloured, flocculent precipitate was present in the liquid. This was filtered off, dried and weighed (0·1620 gram). The liquid after filtering was almost colourless. It was neutralised to litmus paper with barium carbonate, filtered clear from the precipitate of barium sulphate, and evaporated to dryness under reduced pressure (40 mm.). It was found in a preliminary experiment that alkalinity developed during the concentration. This appeared to be due partly to traces of sodium carbonate in the barium carbonate used. A few drops of methyl-red were therefore added to the distilling flask, and the liquid during concentration was kept neutral to this indicator by repeated addition of N/10-sulphuric acid. The residue from the distillation was extracted under reflux with methyl alcohol, free from acetone. After being filtered from insoluble barium and sodium sulphates, and decolorised by boiling with a small quantity of animal charcoal, the methyl-alcoholic solution was evaporated in a current of dry air at a low temperature. Crystals soon formed on the sides of the vessel, and the residue after evaporation of the methyl alcohol was completely crystalline and almost white. It weighed 9·718 grams, and on analysis gave the following figures :—

			Mean.
Moisture (by drying in water-oven) . . .	$3\cdot36$	}	$3\cdot28$ per cent.
,, (by sp. gr. of 10 per cent. solution) .	$3\cdot20$		
Ash		$1\cdot53$	,,
Glucose (by polarimeter)	$94\cdot73$	} $94\cdot57$	,,
,, (by copper reduction) . . .	$94\cdot41$		
		$99\cdot38$	,,

On recrystallisation from absolute alcohol, the residue gave a large crop of white crystals, m.p. $144°$ to $145°$ (uncorr.), and a glucose-phenylosazone, m.p. $204°$ to $205°$ (uncorr.). Allowing for the moisture and ash in the original cellulose, and for the small quantity ($0\cdot162$ gram) of material which was not dissolved by the acid, the yield of crystalline glucose, calculated from the analysis of the crude product, amounted to $90\cdot67$ per cent. of the theoretical quantity. No other product of hydrolysis could be detected either in the barium sulphate precipitate or in the distillate from the evaporation. It is possible that slight losses of sugar may be due to incomplete washing of the voluminous barium sulphate precipitate. Small amounts may also be carried over mechanically during the distillation of the liquid under reduced pressure, or removed by the treatment with animal charcoal. These points are being further investigated.

THE CONSTITUTION OF CELLULOSE. I. THE ACETOLYSIS OF ETHYL CELLULOSE.

K. Hess and W. Wittelsbach (Zeitsch. Elektrochem., 1920, **26**, 232-251).

This paper contains a critical account of the older formulæ proposed for cellulose. The idea that cellulose is based on lævoglucosan is discounted by the observation that ethyl cellulose, on distillation, gives no ethyl-lævoglucosan. The fact that lævoglucosan can be obtained both from cellulose and starch

is considered merely to show that these substances contain dextrose residues of the same configuration as dextrose itself. The authors therefore propose a formula in which the hydroxyl groups of a dextrose, or cellobiose nucleus are etherfied by molecules of dextrose (or cellobiose), the analogy of the tannins (E. Fischer) and some of the disaccharides (Haworth and Leitch, *J. Chem. Soc.*, 1918, **113,** 188 ; 1919, **115,** 809 ; Irvine and Dick, *ibid.*, 1919, **115,** 593) being given in support.

A review of the work of Ost and Madsen and a repetition of their experiments leads the authors to conclude that the maximum yields of cellobiose octoacetate and of dextrose pentacetate, obtainable from 100 grams of cotton (air dry) are 62 and 120 respectively. Of the numerous possible unit formulæ based upon the authors' conception as given above, the following is adopted—

$$CH_2OX . CHOX . CH . (CHOX)_2 . CHOX$$

$$O$$

where X represents the residue—

$$CH_2OH . CHOH . CH . (CHOH)_2 . CH$$

$$O$$

This formula would require the production of 64·2 per cent. of cellobiose octoacetate, and 125 of dextrose pentacetate per cent. of the cellulose, in close agreement with the maxima quoted, while other possible formulæ give widely varying values. The name 'celluxose' is suggested for the unit formula above, 'celluxose' being regarded as identical with hydrocellulose. Cellulose itself is taken as a condensation product of multi-celluxose groupings. The researches of Stern (*J. Chem. Soc.*, 1904, **85,** 336) and Ost (loc. cit.) are adduced in support of the view that little or no elimination of water takes place during this condensation. The authors

assume therefore that the union between the celluxose molecules must be through the residual valencies of the hydroxyl groups.

The celluxose-residual-valency hypothesis is held to explain (1) the great dissimilarity between cellulose and its esters and products derived from it by the action of acids, bases, cuprammonium and zinc chloride solutions.

In all these reactions degradation to celluxose takes place, and the product obtained is a derivative of this substance and not of cellulose.

(2) The disintegrating action of zinc chloride, etc.—it is well known that alcohols, dextrose, etc., readily form compounds with metallic salts. With cellulose we have the alcohol celluxose using its residual valency preferably in the direction of combination with zinc chloride with consequent disruption of the cellulose complex.

An extension of the hypothesis regards the physical arrangement of celluxose molecules in the complex as similar to that of cellulose itself, viz. in the form of a hollow thread. It is therefore not impossible for the residual valency linking to be broken down by mechanical means (Fort), giving a constitutional change less profound than that produced chemically, but with loss of structural character.

(Compare further, Hess, *Zeit. angew. Chem.*, 1921, **34,** 449.)

Although ethyl cellulose does not appear to give an ethyl-lævoglucosan on distillation under 10 mm. pressure, O'Reilly (*Helv. Chim. Acta*, 1921, **4,** 616) claims that by distillation of a particular one of a series of methylated celluloses, viz. one with OMe = 28 per cent., a distillate was obtained (amounting to 50 per cent.), which consisted entirely of methylated derivatives. The most volatile portion of these consisted of a substance agreeing with the composition of dimethyl lævoglucosan which was hydrolysed to a dimethyl-glucose, ' thus confirming
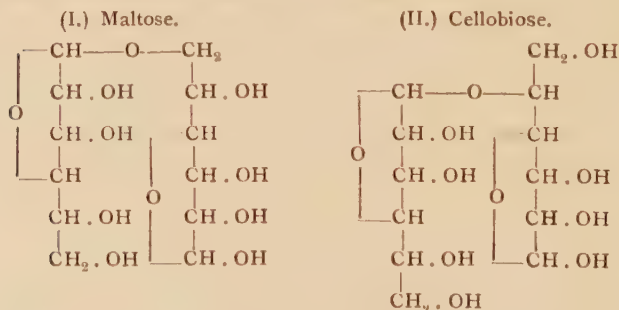
G 2

Pictet and Sarasin's conception of the existence of the lævo-glucosan group in the cellulose complex.'

CELLOBIOSE (CELLOSE).

W. N. HAWORTH and E. L. HIRST (J. Chem. Soc., 1921, **119**, 193).

The relation of this sugar to cellulose is of a similar order to the relation of maltose to starch. During the degradation of cellulose by bacteria, for example, the intermediate formation of cellobiose has been observed (Pringsheim, *Zeit. physiol. Chem.*, 1912, **78**, 266).

The exact mode of linking together of the two glucose residues in cellobiose, hitherto obscure, has now been determined and the following formulæ are given :—

(I.) Maltose.   (II.) Cellobiose.

$$
\begin{array}{ll}
\text{—CH——O——CH}_2 & \text{CH}_2\text{.OH} \\
\text{CH.OH} \quad \text{CH.OH} & \text{—CH——O——CH} \\
\text{O} \quad \text{CH.OH} \quad \text{CH} & \text{CH.OH} \quad \text{CH} \\
\text{—CH} \quad \text{CH.OH} & \text{O} \quad \text{CH.OH} \quad \text{CH.OH} \\
\text{CH.OH} \quad \text{O} \quad \text{CH.OH} & \text{—CH} \quad \text{O} \quad \text{CH.OH} \\
\text{CH}_2\text{.OH} \quad \text{—CH.OH} & \text{CH.OH} \quad \text{—CH.OH} \\
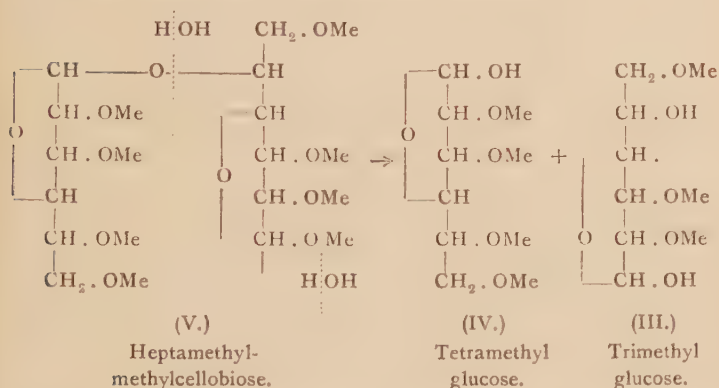& \text{CH}_2\text{.OH}
\end{array}
$$

The method of attack employed for this end was through the methylation of cellobiose by very special devices, a *hepta methyl methylcellobioside*, m.p. 76° to 78°, being obtained (Formula V.).

Of the eight methyl groups protecting the hydroxyls in this compound one is easily eliminated, namely, that protecting the very labile reducing group of the biose.

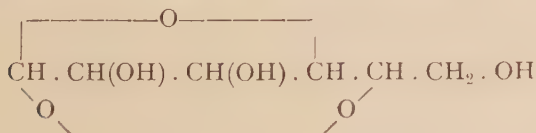On the cleavage of the disaccharide grouping two more

hydroxyl groups are released, namely, the one participating in the union of the two hexose residues. When this was done in the laboratory the products isolated were the butylene-oxide forms (*a*) of trimethyl (Formula III.) and (*b*) of tetramethyl glucose (Formula IV.), the former being identical with that previously isolated from cellulose (p. 90).

These results lead to the following formulæ :—

$$
\begin{array}{ll}
& \text{H.OH} \qquad \text{CH}_2\text{.OMe} \\
\text{—CH——O.———CH} & \\
\quad | \qquad\qquad\qquad | & \\
\quad \text{CH.OMe} \qquad \text{CH} & \\
\text{O} \quad | \qquad\qquad\qquad | & \\
\quad \text{CH.OMe} \qquad \text{CH.OMe} & \\
\quad | \qquad\qquad \text{O} \quad | & \\
\text{—CH} \qquad\qquad\qquad \text{CH.OMe} & \\
\quad | \qquad\qquad\qquad | & \\
\quad \text{CH.OMe} \qquad \text{CH.O Me} & \\
\quad | \qquad\qquad\qquad | & \\
\quad \text{CH}_2\text{.OMe} \qquad\quad \text{H.OH} & \\
\end{array}
$$

		—CH.OH	CH$_2$.OMe
		CH.OMe	CH.OH
	O	CH.OMe +	CH.
		—CH	CH.OMe
		CH.OMe	O CH.OMe
		CH$_2$.OMe	—CH.OH

(V.)   (IV.)   (III.)

Heptamethyl-   Tetramethyl   Trimethyl

methylcellobiose.   glucose.   glucose.

and further considerations of optical properties make it almost certain that cellobiose is glucose β-glucoside. [*N.B.*—The formula (II.) for cellobiose has been confirmed by the work of Bergmann and Karrer, *Chem. Zentr.*, 1921 (iii), 214.]

The authors claim that the evidence in its bearing on the constitution of the cellulose complex, points strongly in favour of a 'structural linking for part of the glucose constituent. This part is the glucose fragment linked with other residues through both the reducing group attached to the fifth carbon atom from the reducing end of the hexose chain :

$$
\begin{array}{l}
\text{|————O————} \\
| \qquad\qquad\qquad\qquad | \\
\text{CH.CH(OH).CH(OH).CH.CH.CH}_2\text{.OH} \\
\quad \searrow \qquad\qquad\qquad\qquad \nearrow \\
\quad \text{O} \qquad\qquad\qquad\qquad \text{O}
\end{array}
$$

This mode of linking is probably largely represented in the structure of the cellulose molecule.' This is at variance with the polymerised lævoglucosan conception (Sarasin).

A very convenient method for the preparation of cellobiose octa-acetate and of cellobiose is given in detail.

THE METHYLATION OF CELLULOSE.
PARTS I. AND II.

W. S. Denham and H. Woodhouse (J. Chem. Soc., 1913, **103**, 1735 ; 1914, **105**, 2357).

The researches of Willstätter and of Ost (1913) seem to have established definitely that the cellulose molecule is composed wholly of dextrose residues. While further study of the products of acetolysis may yield an insight into the manner of linking of the dextrose residues in these derivatives and therefore in the parent substance, another method of attack is suggested by the results of the researches of Irvine and his collaborators on the constitution of the methylated monosaccharides.

If cellulose were methylated, subsequent cleavage of the whole molecule should yield methylated dextroses in which the methoxyl groups represent hydroxyl groups of the original cellulose complex, so that the nature of the linkings would be determined to an extent dependent on the degree to which the cellulose had been methylated before the cleavage of the molecule.

Cellulose was left for two or three days with 3 to 4 times its weight of sodium hydroxide of 15 to 17 per cent. strength, roughly as $C_6H_{10}O_5 : NaOH$. The requisite amount of dimethyl sulphate necessary to react with the alkali was then added. The whole treatment was repeated. The progressive nature of the reaction is shown in the following table :—

Concentration of sodium hydroxide.	Percentage of methoxyl after treatment.				
	1st	2nd	3rd	4th	5th
I. 15 to 18 grams per 100 c.c.	8·5	19·7	23·3	25·5	24·6
II. 17 grams per 100 c.c.	5·3	11·5	14·0	18·7	20·7

These non-homogeneous methylated celluloses are fibrous, becoming more horny with increasing methylation. The initial products are soluble in cuprammonium, the later ones not so. They can be acetylated (Lilienfeld, Fr. pat. 447,974, Jan., 1913 ; also *J. Soc. Chem. Ind.*, 1913, **32**, 420), although analysis shows that demethylation and perhaps degradation, takes place simultaneously. They also undergo the xanthate reaction, which is of interest in relation to the question of the relative reactivity of the hydrogen atoms of cellulose, 'for if the most reactive hydrogen atom of the unit $C_6H_{10}O_5$ is replaced in ordinary viscose from cellulose by the . CS . SNa group, and in the methylated cellulose by the methyl group, it is evident (if the compositions of the xanthates are similar) that the xanthate from ordinary cellulose must involve, in its formation, a different hydrogen atom from that which is concerned in the formation of the xanthate from the methylated cellulose.'

For the hydrolysis, Willstatter's method (40 per cent. hydrochloric acid, at 0° and room temperature) was found extremely suitable. With a product containing 25 per cent. of methoxyl from 20 to 50 times the weight of acid was employed. The substances finally obtained were—

(1) An amorphous monomethyl glucose or a mixture of monomethyl glucoses.

(2) An amorphous dimethyl glucose or a mixture of these.

(3) A crystalline trimethyl glucose.

(4) A trace of crystalline matter resembling tetramethyl glucose.

The amounts of (2) and (3) were approximately equal. The weight of (3) separated in the crystalline form was

approximately 10 per cent. of the weight of the hydrolytic product though more was present in the residual syrups.

To isolate the sugars the syrup obtained after the removal of the hydrochloric acid, by distillation under reduced pressure, was extracted with acetone. The portion most soluble in acetone on the addition of ether gave a precipitate which could be crystallised, and consisted of trimethyl glucose, m.p. 110° C., $[\alpha]_D$ (in acetone) initial $+$ 101°, final $+$ 69·52°.

After separation of the trimethyl glucose the residue was heated in a tube with a 0·25 per cent. solution of hydrogen chloride in methyl alcohol for thirty-two hours. The acid was removed and the syrup distilled. In this way two fractions, each having the composition of a dimethyl glucose, were isolated.

METHYLATION OF CELLULOSE. PART III. HOMO-GENEITY OF PRODUCTS AND LIMIT OF METHYLATION.

W. S. Denham (J. Chem. Soc., 1921, **119,** 77).

The author finds that the immediate necessity for the stage at which his researches have now arrived is the preparation of a cellulose methyl ether of maximum OMe content in which the cellulose complex has undergone the minimum of degradation : and further, the examination of the limiting and intermediate ethers and their degradation products.

For such preparations the method previously described (treatment repeated alternately with methyl sulphate and sodium hydroxide solution) has yielded a product containing 44·6 per cent. of OMe. Trimethyl cellulose, $C_9H_{16}O_5$, requires 45·6. That these ethers still retain a high degree of complexity is shown by the almost complete absence of copper reducing property and the retention of the fibrous structure : further, the

displacement of hydrogen by methyl groups does not confer solubility in solvents such as alcohol, acetone or chloroform.

The solubility of methylated cellulose in Schweitzer's reagent, however, decreases as the OMe content increases, products which contain about 40 per cent. being insoluble. This affords a method of examining the homogeneity of any preparation. Several of these left a residue which contained a higher content of OMe than the untreated substance. The most homogeneous product examined was one in which an ethereal solution of methyl sulphate was employed, and the best yields also were given when ether was used. A preparation containing 42 per cent. of OMe was quite insoluble in Schweitzer's reagent and also in the above-mentioned solvents and was therefore so far homogeneous.

The author concludes that the limit of methylation is in the neighbourhood of that required for a trimethyl cellulose, and that a methyl cellulose of this limiting methoxyl content can be prepared which is representative of the whole of the original cellulose. The trimethyl glucose is derived from this substance and not from a more highly methylated cellulose.

TRIMETHYL GLUCOSE FROM CELLULOSE.

W. S. Denham and H. Woodhouse (J. Chem. Soc., 1917, **111**, 244).

The most characteristic derivative obtained by the hydrolysis of methylated cellulose is the crystalline trimethyl glucose. This sugar differs from the isomeric methyl glucoses in two ways. The latter very rapidly reduce potassium permanganate in the cold (*J. Chem. Soc.* 1915, **107**, 256), and the conversion of tetramethyl γ-glucose into the corresponding methyl-glucoside proceeds much more rapidly than that of tetramethyl glucose under parallel conditions (*ibid.*, p. 521).

The trimethyl glucose from cellulose, as well as the crude uncrystallisable syrups also obtained, which probably consist of a mixture of mono-, di- and trimethylated glucoses, do not show these properties, and it appears that methylated syrups from cellulose are to be classed with the butylene-oxide type of glucose.

'This view, whilst in harmony with that of Fischer (*Ber.*, 1914, **47**, 1983), regarding cellobiose, which, from its behaviour towards enzymes, he considers to stand nearer to the crystalline methylglucosides, cannot, meanwhile, be claimed to imply necessarily the existence of the same linking in the parent cellulose, for rearrangements of the oxygen linkings on, or after hydrolysis, are conceivable, with the formation of more, from less stable, systems. According to Haworth and Law (*J. Chem. Soc.*, 1916, **109**, 1314) transformation may occur on the hydrolysis of sucrose, the first liberated γ-fructose, evidence for the existence of which is discussed by Irvine and Robertson (*ibid.*, p. 1305), afterwards undergoing transformation into ordinary or butylene-oxidic fructose.'

There are, theoretically, four pairs of isomeric trimethyl glucoses possessing the butylene-oxide structure, but of these, two are at once excluded as possible formulæ for the trimethyl glucose from cellulose.

'The selection lies therefore between the two following formulæ :—

(III.) $CH . OH . CH . OMe . CH . OMe . CH . CHOH . CH_2 . OMe$

O————

(IV.) $CH . OH . CH . OMe . CH . OH . CH . CH . OMe . CH_2 . OMe$

$— O —$
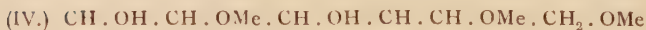
and the trimethyl glucose might be obtained by rearrangement from a sugar containing an amylene-oxide ring, which would

give (III.), or from one containing a propylene-oxide ring, which would give (IV.).'

The paper contains an account of an experiment made in an attempt to discriminate between the two formulæ. The result was not altogether conclusive, but it indicated that formula (III.) above best represents the structure of trimethyl glucose derived from cellulose.

THE ACTION OF HEAT ON CELLULOSE AND STARCH.

(*a*) **Researches on Cellulose and Starch.**

J. SARASIN (Archiv. sci. phys. nat., 1918, (iv.), **46**, 5).

(*b*) **Distillation of Cellulose and Starch Under Reduced Pressure.**

A. PICTET and J. SARASIN (Helv. Chim. Act., 1918, **1**, 87, 226; C. R., 1918, **166**, 38).

The last contribution contains a connected account of the work of what we may denominate the Swiss group of chemists, up to the date of publication (1918).

(*a*) (Sarasin.) Both cellulose and starch on distillation with zinc dust at ordinary pressure gave the following products, no points of difference being detected between them:—

(1) Gases: H_2, CO, CO_2, C_2H_4, CH_4.

(2) Aldehydes and Ketones: acetone, methylethylketone and homologues.

(3) Furfural derivatives: furfurane and its α-methyl-, 2, 5 dimethyl, trimethyl, and tetramethyl-derivatives.

(4) Phenols: phenol, cresol.

(5) Acetic acid; a body $C_{12}H_{14}O$; trace of toluol.

(*b*) (Pictet and Sarasin.) When heated alone under a pressure of 12 to 15 mm. decomposition begins at 210°, starch and cellulose behaving exactly alike and yielding the following products per cent. :—

	Cellulose.	Starch.
Semi-crystalline mass .	45	45
Aqueous liquid . . .	32	39
Gas and loss . . .	13	6
Residue	10	10

The semi-crystalline mass proved to be lævoglucosan (Tanret, 1894), a body of m.p. 179·5°, very soluble in water and alcohol, but insoluble in ether, chloroform, etc., $[\alpha]_D - 66°$.

It does not reduce Fehling's solution and is not fermentable. Warmed with acids, it yields *d*-glucose. It gives a triacetate, m.p. 110°, and a tribenzoate, m.p. 200° C.

The products of hydrolysis of starch, viz. dextrin, maltose, and glucose, gave traces only of lævoglucosan on dry distillation. The authors conclude therefore that the lævoglucosan complex exists preformed in the starch and cellulose. The question of the configuration of lævoglucosan therefore becomes important.

Lævoglucosan treated with polymerising agents very readily polymerises, giving not, it is true, cellulose or starch, but a dextrin. This change takes place on simple heating, but much more completely in the presence of platinum black at 180° C. The product, a white powder, dries up from solution in vitreous masses, its molecular weight is approximately 650, corresponding to a formula $(C_6H_{10}O_5)_4$. It is not coloured by iodine, in which respect it differs from amylo- and erythro-dextrin, resembling rather the achroo-dextrins.
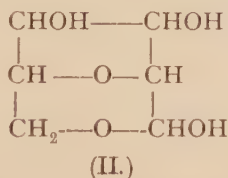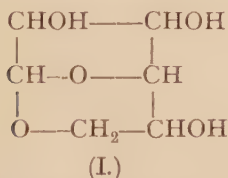
(*c*) (Pictet and Castan.) On Glucosan:

By heating glucose at 150° C. under 14 mm. pressure, there distils over a substance identical with the glucosan of Gélis (1860).

It crystallises readily from methyl alcohol, m.p. 108° to 109°, $[a]_D$ + 69°, benzoate m.p. 75°. It does not reduce Fehling's solution, but shows remarkable additive properties. Thus, it is easily transformed into dextrose on boiling with water; with phenyl hydrazine it gives phenyl glucosazone and with methylic alcohol containing a trace of hydrochloric acid, it yields α-methylglucoside (*C. R.*, 1920, **171**, 243).

THE CONSTITUTION OF LÆVOGLUCOSAN.

A. Pictet and M. Cramer (Helv. Chim. Act., 1920, **3**, 640).

A reasoned experimental study of lævoglucosan leads the authors to recommend the formula (I.)—

$$\begin{array}{ll} \text{CHOH——CHOH} & \text{CHOH——CHOH} \\ \quad| \qquad\quad | & \quad| \qquad\quad | \\ \text{CH--O——CH} & \text{CH ——O— CH} \\ \quad| \qquad\quad | & \quad| \qquad\quad | \\ \text{O——CH}_2\text{—CHOH} & \text{CH}_2\text{--—O—-CHOH} \\ \quad\quad\text{(I.)} & \quad\quad\text{(II.)} \end{array}$$

instead of formula (**II.**) previously given and frequently quoted in the literature in arguments connecting this substance with a possible furfurane ring in cellulose.

THE METHYLATION OF STARCH.

P. Karrer (Helv. Chim. Act., 1920, **3**, 620).

Criticising the celluxose theory of Hess, the author thinks that a clear picture of the building up of polysaccharides can be obtained without such special hypothesis. A crystal of silver can be made into a colloidal solution though each particle contains at least 125 atoms. A 'molecular' solution of silver cannot be produced, but its water-soluble derivatives

have a determinate molecule. The author conceives starch (and cellulose) as such 'crystalloids.' In colloidal solution they are molecular aggregates, but in the water-soluble derivatives, depolymerisation has taken place, and a determinate molecule results.

To test this he has prepared three methylated starches with the following composition and properties :—

OMe groups per $C_6H_{10}O_5$ unit.		Solubility in		Iodine Reaction.
	Water.	Alcohol.	Chloroform.	
I. 1·0	+	−	−	Red-violet.
II. 1·5	+	±	−	Yellow-brown.
III. 2·0	+	+	+	Yellowish.

These properties indicate depolymerisation to the molecular unit. The molecular weight of (III.) indicated a starch molecule of between 1000 to 2000, so that only a relatively small number of monosaccharide groups are combined together.

ON THE CONSTITUTION AND CONFIGURATION OF GLUCOSIDES.

P. KARRER (Helv. Chim. Act., 1920, **3,** 258).

Pictet and his co-workers (*ibid.*, 1919, **3,** 698) have shown that lævoglucosan is obtained on distillation of many glucosides in a vacuum, such as salicin, arbutin, etc. They assume that these substances, which are all β-glucosides, are direct derivatives of lævoglucosan.

Commercial dextrose consists largely of α-glucose and on distillation yields only traces of lævoglucosan. Karrer, however, finds that β-glucose gives lævoglucosan in amount comparable with that given by starch. He concludes—

(1) That lævoglucosan is a conversion product of β-glucose and certain β-glucosides, and results from them during vacuum distillation. That the atomic grouping of lævoglucosan is the

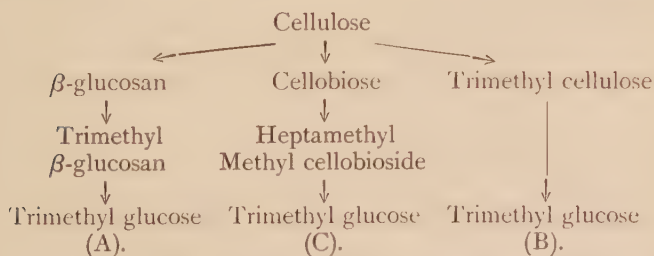basis of the configuration of starch and cellulose is possible, but not necessarily the case.

(2) Starch and cellulose contain, to some extent at least, β-glucosidic linkages.

THE RELATIONSHIP OF *l*-GLUCOSAN TO *d*-GLUCOSE AND TO CELLULOSE.

J. C. IRVINE and J. W. H. OLDHAM (J. Chem. Soc., 1921, **119,** 1744).

The claims of Pictet, that both cellulose and starch are polymerides of glucosan is strongly criticised in this paper. The complexity of the changes undergone by carbohydrates on heating is notorious, and the authors say that, as in the dry distillation of cellulose acids are also produced, it is probable that hydrolysis to β-glucose is an essential factor—this sugar then distilling forward as anhydride—in fact they have now proved that *l*-glucosan is 1 : 6-β-glucose anhydride and therefore employ the term β-glucosan instead of *l*-glucosan.

The experimental portion of the work is based on the transformations shown in the left-hand side of the following scheme :—

Cellulose

β-glucosan   Cellobiose   Trimethyl cellulose

Trimethyl   Heptamethyl
β-glucosan   Methyl cellobioside

Trimethyl glucose   Trimethyl glucose   Trimethyl glucose
(A).   (C).   (B).

If A and B are identical the glucosan unit *is* present in cellulose and Pictet's polymerisation theory is supported ; but if A and B are isomeric quite the contrary. The authors find that

A is not identical with B, but that it is the sugar previously prepared from methylglucoside and from maltose (*J. Chem. Soc.*, 1919, **115**, 593, 809). The identity of B and C (*ibid.*, 1921, **119**, 193) shows clearly that the cellobiose residue is an essential part of the cellulose complex. The properties of A and B given briefly emphasise their differences :—

Properties.	A	B
Properties . . .	Liquid, b.p. 160° /0·2 mm.	Cryst., m.p. 123°
On heating . .	Gives trimethyl glucosan	Stable
β-methylglucoside .	Crystalline solid	Liquid
Can be prepared from	Maltose, but not cellobiose	Cellobiose, but not maltose

The constitution of β-glucosan—on oxidation with nitric acid the trimethyl glucose A is converted into a lactone, the investigation of which shows that A must have the formula—

$$—————O——————$$

$$OH . CH_2 . CH(OMe) . CH . CH(OMe) . CH(OMe) . CH . OH$$
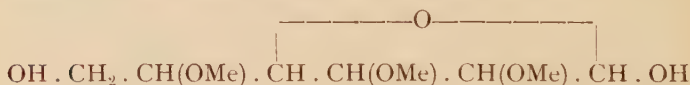
It follows that in the formation of glucosan from glucose, dehydration involves the reducing group and also the terminal primary alcoholic group. This leads to the formulæ—

α-glucosan.   β-glucosan.
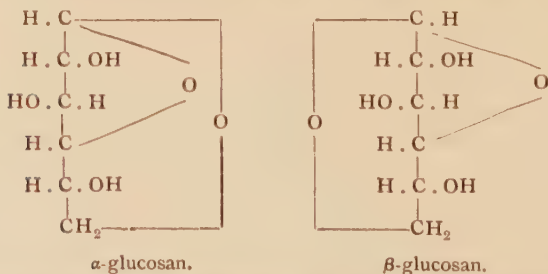
according as the sugar reacts in its α- or β- form. The β- constitution is established by the authors for *l*-glucosan, the formula given being thus identical with that of Pictet (p. 93).

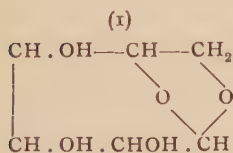' Pictet's views are inconsistent with the facts that starch

can be degraded to maltose and cellulose to cellobiose. It is now established that the conversion of cellulose into β-glucosan is essentially a dry distillation of β-glucose.'
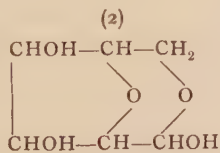

THE CONSTITUTION OF CELLULOSE.

H. HIBBERT (J. Ind. Eng. Chem., 1921, **13**, 256).

This study opens with a brief account of the most recent systematic researches of Ost, Willstätter, Denham and Wood-house, Pictet and Sarasin, which in the author's view establish beyond question the quantitative relationship existing between cellulose and dextrose, notwithstanding certain arguments to the contrary (M. Cunningham, and Cross and Bevan, *J. Chem. Soc.*, 1918, **113**, 173, 182).

This main thesis is then developed first through a critical bibliography in order of date, reviewing the formulæ for the assumed unit group (C_6) proposed by Tollens, Cross and Bevan, Vignon, Green, Barthelemy, with the evidence upon which they are based by their authors and a present *exposé* of their weak points. From these and earlier attempts the author retains two as of more probable value, and contrasts with these his own as below :—

(1)

$CH.OH——CH——CH_2$

| | | O O

$CH.OH.CHOH.CH$

Vignon.

(2)

$CHOH—CH—CH_2$

| | O O

$CHOH—CH—CHOH$
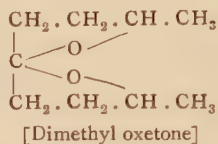
Green.

(3)

CH_2OH

|

$CH——CH——O$

| O |

$CHOH.CHOH CH$
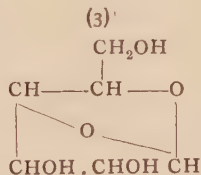
Hibbert.

In (1) and (2) the aldehydic 'O' is engaged by intra-molecular union with two OH groups of a dextrose unit, but (3) differs by its primary alcoholic group.

IV,   H

The condensation of $\gamma\gamma'$ dibromovalerone on boiling with water to

$$CH_2 . CH_2 . CH . CH_3$$
$$C \overset{O}{\underset{O}{\diagup \diagup}}$$
$$CH_2 . CH_2 . CH . CH_3$$

[Dimethyl oxetone]

is adduced in support of the intramolecular condensation, which, if occurring in the $\gamma\delta$ position, would give the analogue in question.

Some experimental evidence as to this type of condensation, i.e. in the region of polyhydroxy- compounds is obtained in preparing nitric esters from glycerol-dextrose, and glycol-dextrose mixtures, in which two OH groups of the total 8 or 7 respectively, disappear; but the critical points as between intramolecular condensation of the dextrose, or its condensation with the alcohol, is left undetermined.

From the unit group the author derives his polymerised complex, i.e. cellulose as
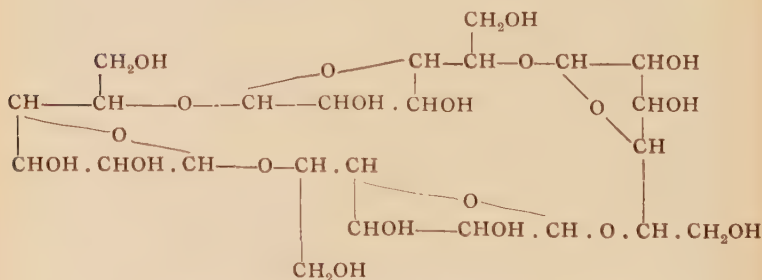
and notes that this formula should satisfy the categorical points of reactivity on which Green based his formula (*J. Chem. Soc.*, 1906, 811; *Rev. Gen. Mat. Col.*, 1907, **2**, 130), and, in addition, the formation of 1, 2, 5-trimethyl glucose (Denham and Woodhouse), of lævoglucosan (Pictet), and of cellobiose (Ost),

as well as the ascertained general relationship of cellulose to starch.

These transformations are discussed in detail, and with critical reference to the author's formulation of the unit groups and the polymerised complex.

*   *   *   *   *   *   *

This contribution to a major problem we have already noticed, with the implied criticism that it is sectional in aim and ignores the wider aspect of the subject. But as a sectional contribution it fails to take into account a number of factors of the problem.

The treatments involved in the resolution of the cellulose system to proximate groups $(C_{12} - C_6)$ are severe, and must determine constitutional changes; thus it is evidently possible that there could be rupture of a ketonic unit such as to change the relative position of the critical CO group. A ketonic constitution is not only a direct inference from Fenton's researches, but it is also an implied inference from the investigations of Will and Lenze on the comparative esterification (nitrates) of the simpler aldoses and ketoses. Further, we have recorded typical cases of esterification of celluloses, of which the quantitative data point to loss of H_2O independently of the ester reaction, and in the case of cellulose nitrates prepared from (normal) cotton cellulose, the yields of product are in many cases divergent from that calculated from their composition (N, i.e. NO_3). The number of definitive OH groups of the assumed (C_6) unit is therefore still a problem, not yet resolved by reaction. In the author's unit group, two of the OH groups are involved in the intramolecular condensation, with the aldehydic oxygen. This assumption, moreover, leaves the polymerisation dependent upon the relatively feeble linking by residual affinities, and although in this formula picture of the cellulose complex the author is confirmed by Hess and Wittelsbach, a constitutional bond of this order is at variance, as

H 2

we hold, with all the special chemistry of cellulose, both in its positive reactivity and its negative qualities of resistance to attack.

Assuming for the moment the claims for quantitative resolution of cellulose to dextrose, and the general thesis that quantitative resolution to groups of known configuration must warrant their reintegration as a constitutional formula of the original substance, there is little choice as to the particular type of intramolecular bond if we are limited to the established analogues of structural chemistry based on residual affinities or tetravalent oxygen.

Any such formula or view appears to us to conflict with much that is established for cellulose as a homogeneous system reacting as a chemical individual on the one side, and on the other in regard to the specific characteristics of inertness or resistance to attack. Even if we take the evidence of the mechanism of resolution in a critical case, viz. the attack of sulphuric acid involving a close study of the stages of resolution, the systematic investigations of A. L. Stern long since (1894) established that no dextrose is formed until the resolution is advanced to stages demonstrably far removed from the cellulose region. Moreover, in the investigations cited as evidence, there is no specific estimation of dextrose as such ; in some cases the evidence is merely inferential from the data of cupric reduction, and therefore *a fortiori* in regard to the particular point. The later systematic investigations of M. Cunningham, in which both cotton and esparto cellulose were studied, establish, not only the very complex nature of the resolutions, but some definite points in regard to constitution of ultimate groups, e.g. particular basic and acid functions of OH groups, and constitutional changes affecting the yield of furfural (esparto) which involves a probable change of position and function of the CO groups.

On these results and a general survey of the records of the

researches of Flechsig, Ost, König, Willstätter, we again vindi-
cate the agnostic position, with a clear recognition of the
paradox involved.

There is no proof of the presence in cellulose of groups of
dextrose configuration, and even in the case of starch, which is
resolved by processes calculated to determine the minimum of
change in the ultimate groups, it is not established that a
polylævoglucosan constitution is a full, or even necessary ex-
planation, of its reactivity in relation to these processes.

The multiple aldosan complex which is postulated for both
bodies, or groups, leaves them undifferentiated—save on minor
points, and contains no suggestion of the cause of their strik-
ing divergence in all that determines their characteristics as
individuals.

In regard to the specific point of difference of the author's
formula from those of Green and Vignon, viz. the primary
alcoholic group, some confirmation is furnished by our studies
of partial acetylation, and the hetero-cyclic configuration is to
be considered in relation to the characteristic fluorescence of
cellulose and certain of its esters.

On the other hand, the resistance of cellulose to oxidation in
the sense of fixation of oxygen, argues against the presence of
primary alcoholic groups.

It should be noted that we have much to learn in assigning
to the OH groups their true gradation of reactivity and this
requires a critical study of structural changes accompanying
reaction.   These changes may be those of visible structure, or
changes of viscosity of solution in the case of soluble derivatives.
Changes of either order are noted (a) in the controlled pro-
gressive acetylation (zinc chloride process at 40° to 50°), (b)
in cuprammonium solutions which are exposed to oxygen
and to light.   In the former our observations indicate a
diacetate (C_6) as normal limit : beyond that point the structural
changes are considerable, and the cellulose regenerated from

the esters show, moreover, that no synthetic reaction of cellulose can be brought through a true cycle, Cellulose (A)→ Cellulose ester→ Cellulose (B) : the ' B ' form is degraded in relation to the ' A.'

In regard to the marked changes (*b*) in cuprammonium solutions, these have not been fully investigated.

The oxidation of the ammonia to nitrite is well established, but it has not been shown what, if any, part is played by the cellulose complex : but in the general complex of ions the cellulose OH groups are no doubt labile and tend to migrate with rearrangement. The investigation of the forms of cellulose regenerated from such solutions would determine the character of such changes as affecting the ultimate groups.

CHAPTER IV

CELLULOSE AS AN ORGANIC COMPLEX

THE cellulose of systematic chemistry is a somewhat arbitrary and unreal conception, and it becomes necessary to correct the too narrow view implied in the general treatment of the preceding section, by setting out a number of characteristics of reactivity which are certainly correlative with its unique position and functions in the natural world. Some of these are specifically expressive of properties of component groups of cellulose as a chemical individual, and in due course will be taken into account in the critical adoption of a constitutional formula : others are more evidently related to the colloid aggregate, having an organised and much differentiated structure, and retaining in other ways the impress of vital origin.

It will perhaps give a clearer definition to the wider conception about to be developed if we begin with a concrete case, and an investigation arising out of our working hypothesis of ' reactive continuity of the cellulose aggregate.' In extension of our knowledge of the ' viscose ' reactions (xanthogenic-hydrate-esters) it was necessary to examine limiting cases, and as regards the first phase, interaction of cellulose and NaOH, a limiting case was already defined by various investigations of the mercerisation reactions. In treating bleached cotton yarns with caustic soda solutions of concentrations diminishing from 15 per cent. NaOH, there is a rapid fall in the visible and measurable structural modifications, and in the region 11 to 9 per cent. they become fractional. This defines a limit of reaction of the first or alkali-cellulose phase.

But cotton cellulose impregnated with 9 per cent. solution (1 to $2\frac{1}{2}$ times its weight) and exposed to carbon disulphide, reacts with marked results : with only a fractional production of xanthate the cellulose acquires a disproportionate capacity for hydration, and in washing, the avidity of the new product for water produces a swelling of the individual fibres up to 10 to 60 diameters, in proportion to the relative weight of NaOH to cellulose in the 'alkali cellulose.' The structural changes are illustrated by the subjoined photographs.[1]

In a particular experiment, a normal cellulose (gun-cotton, normal) was treated with the following results :—

	Per cent. of the cellulose.
Total combined S-xanthate and by-products .	3·4 to 4·0
,, soluble cellulose, as xanthate . . .	1·6 to 2·5

The washed products, hydrate gels, retain a proportion of insoluble xanthate. In a particular experiment the following were estimated :—

Soluble xanthate in terms of soda (NaOH) in combination	0·44 per cent.
Insoluble ,, ,, ,, ,,	0·50 ,,

A measure of the degree of hydration is afforded by the weights of the masses washed and drained under pressure (650 mm.) on a calico filter, these being a large multiple of the original weight of the cellulose. They are much exaggerated in the case of raw cotton (Egyptian cotton sliver).

The following particulars of experiments, with some variations of treatment, are illustrative : 10·0 grams, immersed in 9 per cent. NaOH at 90°, squeezed (*a*) to 30 grams, (*b*) to 25 grams, exposed (cold) to CS_2 ; products washed and drained on vacuum filter.
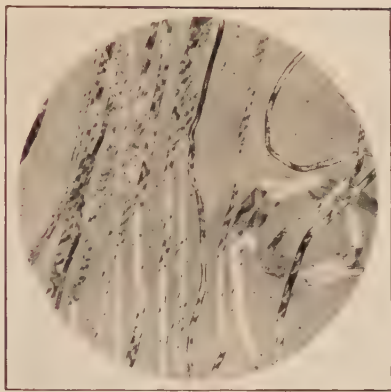
	(*a*)	(*b*)
Weight of washed hydrated mass . .	170 grams.	95 grams.
Soluble cellulose in washings . .	2·9 per cent.	1·8 per cent.
Washed hydrate, treated with 9 per cent.		
NaOH in the cold : dissolved . .	48·0 per cent.	15·0 per cent.

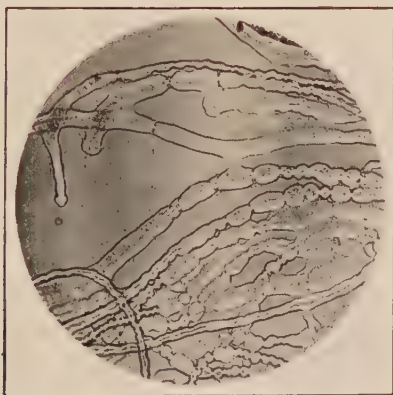[1] Brit. Patent, 126,174 (Appl. 8342/18).

PLATE III.

(a)

(b)

(c)

Hydration process : (a) the first stage ; (b) the same in polarized light ;
(c) second stage.

(*Cross & Bevan : U.K. Patent,* 1918.)

The following is a more exact comparison, i.e. under equal conditions of treatment, of the normal bleached cotton (*a*) (gun-cotton standard) and raw cotton, (*b*) (Egyptian sliver): 10 grams (*a*) and (*b*): digested 16 hours in cold NaOH (9 per cent.), pressed to 30 grams, and exposed to CS_2, proportions varied from 6 to 25 per cent.

After reaction, washed (500 c.c.), and the alkali estimated in washings in regard to ratio of NaOH : NaOH of by-products (sulphocarbonates) as a measure of reaction, the washed cottons were fully drained on a vacuum pump, and the hydrated masses weighed :—

	(1) Blank.	(2) 6·0 per cent. CS_2.	(3) 25 per cent. CS_2.
With bleached cotton—			
(*a*) Residual NaOH per cent.			
of original . . .	86 *	37	0
Weight of washed hydrates .	34 grams	34 grams	45 grams
With raw cotton—			
(*b*) Residual NaOH . .	80 * per cent.	34 per cent.	0·0
Weight of washed hydrates .	40 grams	40 grams	85 grams

(* Loss due to incidental absorption of atmospheric CO_2.)

The treatments have been further varied in respect of the important factors, concentration of NaOH (11 to 5 per cent.), proportion of CS_2 to cellulose (6 to 25 per cent.), duration of reaction (4 to 24 hours). The degree of action measured in the above terms, or by microscopic measurements of individual fibres, is directly proportional to the several factors ; the most important control being the concentration and ratio of the NaOH (9 per cent. solution) to the cellulose.

The following further characteristics remain to be noticed : the hydration effects are reversible. The washed hydrate, freed from residual NaOH by treatment with acetic acid (1 per cent.), reverts to the condition of the original, a particular evidence of which is the unchanged capacity for absorption of atmospheric

moisture. In regard to structural modifications, the exaggeration of dimensions occurs without distortion, the fibre conserves its symmetry, and the reaction was used by W. L. Balls in the demonstration of concentric daily growth rings (Plate I. (*b*), p. 14), so that the reactions appear to reverse the natural dehydration processes of maturation.

To interpret these results in terms of the specific reaction and a stoichiometrical equation, the NaOH combined as xanthogenate—0·94 per cent., i.e. 1·0 per cent. of dry cellulose—representing 1·6 per cent. $C_6H_{10}O_5$ (162), is in the ratio NaOH : $25 \times (C_6H_{10}O_5)$, and this gives no account of the major reaction of hydration, which evidently involves the cellulose aggregate integrally.

Assuming that the synthetic reaction is limited to a group representing a fraction $(\frac{1}{25})$ of a polymolecular unit, it must be then assumed that the group is a key position of a closed unit, the opening of which induces general reaction with water molecules to re-establish equilibrium.

But the hypothetical unit of $25\ C_6$ dimensions has still to be considered in relation to the actual reacting mass. In all reactions of cellulose we have to deal with sensible visible mass ; and a statistical uniformity which appears to justify a stoichiometrical equation—

$$C_6H_{10}O_5 + n \cdot X \cdot OH = n \cdot H_2O + C_6H_{(10-n)}X \cdot O_5$$

may be either a mass average, and in that sense true, or there may be a property of cellulose, that is a constitutional characteristic of the aggregate, tending to promote or facilitate reaction, therefore to the production of uniform products.

As we are dealing with the reaction of hydration (and dehydration) it is proper to consider this in its limiting phases, which are those of the exchanges with atmospheric moisture. The equilibrium in respect of 'moisture of condition' is a characteristic and a constant of the fibre substance, which may be an original cellulose, or a derivative, i.e. either a natural

product or a modified form or synthetic derivative, resulting from some reaction treatment. Extreme variations from the natural form are the esters such as nitrates and acetates, which have characteristic 'moistures' exactly related to the degree of esterification. Thus, from an exhaustive study of the nitrates (cotton cellulose) W. Will established the general empirical expression $H = \dfrac{334 \cdot 3 - 23 \cdot 65 N}{31 \cdot 11 - N}$ where N is the percentage of N, (as $O \cdot NO_2$), in the nitrates. This was established by observations on products in which N varied from 8·5 to 13·15 per cent., and H from 6·16 to 1·42 per cent. in inverse ratio to the degree of esterification.

In the contrary direction, and complementary in respect of the determining factor, Sindall has investigated the influence of the hydration effects in the beating preparation of the celluloses for manufacture into paper (*Paper Maker's Monthly Journal*, June, 1908). The beaten pulps, air dried, retain a higher complement of 'moisture' in direct proportion to the degree of treatment (time × mechanical effect) in the beater. The following figures are selected as illustrative :—

Cellulose from cotton (rags) : boiled (NaOH) and bleached ; beaten and made into sheets of uniform thickness ; air dried ; exposed to saturated atmosphere at 18° and weighed (Series A) ; then exposed to air for 'air drying,' and again weighed (Series B).

	Moisture A.		Moisture B.	
Time of beating.	Per cent.	Increase per cent.	Per cent.	Increase per cent.
4 hrs.	11·2	—	6·4	—
10 ,,	11·7	4·4	6·7	4·7
17 ,,	12·9	15·2	6·8	6·3
25 ,,	12·5	11·6	7·0	9·4
33 ,,	14·0	25·9	7·6	18·7

These figures, as index of a permanent change, were correlated with changes in mechanical properties of the papers (shrinkage in drying, tenacity, elasticity) ; in apparent specific

gravity, and, in regard to the cellulose substance, in dyeing capacity and absorption of soda (NaOH) from solution.

It is evident from the records of researches that chemists tend to regard this 'hygroscopic moisture' as an incident, only to be taken into account in the quantitative statistics of reactions. But in the technology of the cellulose industries, this moisture equilibrium is reckoned with as influencing fundamental properties, as for instance the qualities of papers and textile fabrics, measured in terms of tenacity (breaking strain), elasticity (stretch under strain) and resistance (folding and rubbing tests). [*Cf.*, for example, Barwick, 'Influence of Moisture on the Count of Yarn and the Strength of Cloth,' *J. Soc. Dyers and Col.*, 1913, **29**, 13.]

Although such qualities are properties of structural aggregates, the variations with 'moisture' are definitely related to the fibre substance, and constitute a fundamental property which is independent of external form or structure.

On this comprehensive survey we have a definite picture of 'reactive continuity.' It may be objected that reactions of a system, or aggregate, of discrete molecular units of the type of polydextrose anhydrides, and of variable, as well as large dimensions, would, when reduced to quantitative statistical expression, be interpreted as continuous.

On the other hand, if there is an actual basis of continuous activity in the cellulose mass—a physical linking of units which conditions the transmission of reaction effects, this should be considered in relation to the synthetical reactions, in which the main properties and characteristics of the colloid are maintained, notably, the nitrates and acetates. The ester reaction in simplest terms takes place in the two phases—

$$(1) \ \mathrm{X \cdot OH + H \cdot Y = XHO \cdot HY}$$
$$(2) \ \mathrm{XHO \cdot HY = H_2O + XY}$$
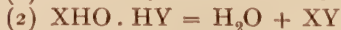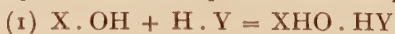
and we suggest, e.g. that in the case of the cellulose nitric acid reaction, the first, or association phase, persists in such

way as to bring into the field of reaction units or molecules at a distance from the plane, or point of surface contact, of cellulose and acid : allowing actual migration of the negative groups or ions, and a definitely graduated attainment of the final equilibrium, with dissipation of the energy of the water reaction. The restraint of reaction thus pictured is based upon the conception of the link of continuity which appears to be a condition, or consequence, of organic (vital) origin : but also upon accumulations of evidence—positive in regard to the properties and reactions of cellulose as such, and negative in regard to all attempts to account for cellulose reactions in terms of molecular quantities.

We should repeat ourselves if we marshalled these points of evidence in regard to the special aspect under discussion.

But there remain to be noticed certain special reactions which must be characteristic of the aggregate and of particular groupings, and therefore to be taken into account in any constitutional formula or picture.

From various investigations of the interaction of cellulose and sulphuric acid, e.g. Stern (1898), M. Cunningham, and Knecht and Thompson (1921), it is evident that the fixation of SO_4H residues is not limited to the reaction with the anhydrous acid (monohydrate). M. Cunningham obtained ester products with the acid $H_2SO_4 . 2H_2O$, which appear to be colloidal hydrate-esters, and Knecht's observations (p. 128) on cotton fabrics treated with the much diluted acid, subsequently squeezed and dried at low temperatures. indicate a probable lower limit. No such reaction taking place with the monoses or bioses (Cunningham), it is to be inferred that cotton cellulose contains a grouping of exceptional basicity : and a constitutional characteristic so specific calls for particular investigation.

Again, in reaction with oxidants, cotton cellulose undergoes changes which are out of proportion to the degree of specific action.

In the case of ozone reactions studied by C. Dorée (see p. 116) fundamental changes in the cellulose aggregate are determined by proportions of the oxidant which are fractional; similarly with hypochlorites, the investigations of Witz (1883) showed 'oxycellulose' effects with minimal proportions of the oxidant ($CaOCl_2$) when intensified by the simultaneous action of carbon dioxide.

In preparing an oxycellulose for inclusion in the series of products investigated by S. Judd Lewis (*ante*, p. 26), the proportion of hypochlorite taken was in the ratio $HClO : 3C_6$; the product showed extremes of differentiation of apparent specific volumes from the normal type, and certain features of change which are seen to be anomalous.

Lastly, the researches of W. H. Gibson (*J. Chem. Soc.*, 1920) on the standardisation of 'cellulose quality' in terms of viscosity of cuprammonium solutions, disclose amongst other anomalies, the powerful effect of air (presumably oxygen) upon these solutions, the viscosity falling to a fraction (1/20th) of the original, on shaking (with air) for 3 hours.

These are features of the special characteristics of cellulose, which immediately or progressively disappear under the severe processes of treatment for resolution to the ultimate groups from which the systematic chemist constitutes the original. It must be admitted that these are violent, in relation to this highly sensitive original: that we have no measure of the progress of these changes in several of the modes of treatment adopted: and only in the case of acetolysis is there any measure of control promising a certain elucidation of the stages.

Even here the control is limited to the more evidently re-active OH groups, and it is clear from the exhaustive investigations (of the esters) that they can be replaced by negative groups without seriously affecting the characteristic properties of the cellulose as a structural colloid.

It is therefore evident that while the 4th oxy-oxygen and the

carbonyl oxygen are more particularly involved in the mechanism of these resolutions and are outside control, we are a long way from any constitutional formula or picture with any claims to reality, comparable with such representations of carbon compounds generally.

It is equally clear that this present objective of systematic chemistry is out of the perspective of the Natural History of the subject.

CHAPTER V

THE series of transformation products included under these general headings have no claim to be considered as individuals of definite identity, and while it is convenient to retain descriptive terms which are generally current, we premise the criticism that the products themselves are, further, essentially variable and each preparation represents a particular state of equilibrium. The problem of the nature of this equilibrium has given rise to considerable discussion in recent times. It is well known that most oxycelluloses (and hydrocelluloses) are resolved by alkaline treatment, leaving a residue without active reducing properties, which closely resembles the original cellulose. As will be seen, a number of workers regard this insoluble residue as identical with cellulose but they ascribe its origin to two different causes dependent on two opposite views of the nature of oxy- and hydrocellulose. According to the first, oxycellulose is considered to be a definite homogeneous oxidation product of cellulose with aldehydic groups (see p. 114, Knecht) resulting from the oxidation of alcoholic residues, and the CHO groupings have been studied in terms of the ordinary reactions of aldehydes, such as the production of cellulose (alcohol) and an acid by the action of alkali according to the well-known reaction

$$2X . CHO + NaOH = X . CH_2OH + X . COONa$$

The second view of the 'oxycelluloses' is that they are mixtures of cellulose (insoluble) with oxycellulose. By the

action of calcium hydroxide solution the oxycellulose is resolved into iso-saccharinic acid leaving unchanged 'cellulose' (Schwalbe). Bancroft regards the oxycellulose as the soluble portion of the oxidised product and the solubility in water or alkalies as merely a function of its degree of dispersion. The cellulose and the oxycellulose may constitute adsorption compounds of varying stability. Tnus Harrison (*J. Soc. Dyers and Col.*, 1912, **28**, 238) regards them as a form of cellulose containing adsorbed reducing bodies.

It is to be noted that though many of the insoluble residues mentioned are claimed to be identical with cellulose on the ground that they possess some of the characteristics of the typical cellulose, the basis of identification adopted is by no means a comprehensive diagnosis of this important question. The identity assumed in some of the records, for example, is not accepted by Ost (p. 126) and his criticism is based on experimental observation.

Hess, in a very original contribution already discussed, regards cellulose as made up of hydrocellulose (celluxose) units, these units being linked together by the residual valency of the oxygen atoms. This linkage is very sensitive in certain directions, especially to acids and oxidants, and a comparatively trifling attack is able to bring about resolution to celluxose which is then further converted to reducing products. We ourselves rather incline to the belief that the cellulose complex contains groupings capable of internal migration, these migrations being of such an order as to amount to synthesis. A minimum proportion of oxygen (or acid) entering into combination at some point in the complex may condition this migration, resulting in the conversion of the cellulose mass affected into oxycellulose (or hydrocellulose). Both ultra-violet light in the presence of air, and ozone, bring about this conversion. In the case of ozone, small quantities of a peroxide are produced which do not greatly increase with continued treatment

although the amount of oxycellulose formed progressively increases.

We proceed to notice the following recent studies of oxy-cellulose formation, though these researches cannot be separated entirely from others on hydrocellulose :—

A HIGHLY OXIDISED CELLULOSE.

E. KNECHT and L. THOMPSON (J. Soc. Dyers and Col.,
1920, **36**, 251).

Nearly all previous methods of preparation of oxycellulose are open to criticism in that (i) if caustic alkalies are employed during oxidation or purification, a portion of the oxycellulose passes into solution, leaving an insoluble part which has practically no reducing properties (e.g. those of Nastjukoff) ; (ii) if mineral acids are used hydrolysis may take place giving products other than oxycellulose. This applies to the oxycelluloses of Witz (bleaching powder), of Vignon (chlorate), of Cross and Bevan, Nastjukoff and Tollens (nitric acid), etc. ; (iii) No measurements have been made of the amount of oxidising agent reacting.

The authors finally decided to use acid permanganate, and claim by this method to have prepared an oxycellulose with more active aldehydic properties, therefore representing a higher state of oxidation, than has previously been obtained, and this without fundamental degradation of the cellulose complex.

The first preparation of which full details are given was made with one atom of oxygen for each $C_6H_{10}O_5$, the very high yield of 94·5 per cent. being obtained.

This oxycellulose was dried at 40° C. and shows no acidic properties. It is so sensitive to alkalies that it gives the intense golden yellow colour with N/100 NaOH solution on boiling, while a 5N solution gives the colour in the cold. No previously

described oxycellulose does this. It is considered to be due to the simultaneous oxidation and reduction of the aldehyde to acid and alcohol.

The alkaline solution on acidification gives a precipitate of 'acid cellulose' which has no reducing properties, but a marked affinity for methylene blue. It is about equal in weight to the insoluble portion, which behaves like cellulose except that it is dyed by methylene blue.

The oxycellulose has no affinity for acid dyes. It gives Schiff's reaction very strongly and reacts with phenyl hydrazines.

It was not found possible to reduce it to cellulose, and its reactions with typical aldehydic reagents, ammonia, hydrocyanic acid, etc., were very indefinite. It absorbs sodium bisulphite very strongly, with rise of temperature, from solutions of 50° Tw.

Reducing Properties.—These are very marked. The copper number is 14·2, and in addition to Fehling's solution, it precipitates cuprous thiocyanate from the cupric salt. Ammoniacal silver nitrate is reduced to silver. Warmed with ferric ferricyanide Prussian blue is precipitated.

In general it exerts its reducing action only in alkaline solution. Thus methylene blue, safranine, rosinduline, crystal scarlet, indigo and indanthrene are reduced under this condition.

A preparation was made using two atoms of oxygen per $C_6H_{10}O_5$. The yield was 93 per cent., but the product became gelatinous on washing and adsorbed the manganous sulphate formed. The portion soluble in alkali was comparatively small; the residue reduced Fehling's solution and formed hydra- zones. Hence this highly oxidised product is not, apparently, acid cellulose, and the second stage of oxidation does not appear to take place at the aldehydic grouping. (Further, *J. Soc. Dyers*, 1922, **38**, 132.)

*   *   *   *   *   *   *

The above investigation is on right lines and an interesting reaction product has been obtained. The following papers

contain a study of the effect of active oxygen in the form of ozone, the system being one of great simplicity : oxygen-water-cellulose only :—

THE ACTION OF OZONE ON CELLULOSE. PART I. ON COTTON. PART IV. CELLULOSE PEROXIDE.

C. Dorée and (in part) M. Cunningham (J. Chem. Soc., 1912, **101**, 497 ; *ibid.*, 1913, **103**, 1347).

THE ACTION OF OZONE ON THE TEXTILE FIBRES.

C. Dorée (J. Soc. Dyers and Col., 1913, **29**, 205).

The action of ozone presents a case of an oxidising agent free from the simultaneous complication of mineral acids or caustic alkalies. Cotton wool when exposed in a dried condition to a current of ozonised oxygen (1·5 per cent. by weight of O_3) acquired a fatty odour, was acid to moist litmus paper and liberated iodine from potassium iodide solution. The last property was lost on heating to 80° C., or by keeping for 14 days ; the acidity, however, was permanent.

These properties pointed to the formation of a cellulose peroxide similar to that mentioned by Ditz (1908), as being produced by the action of ammonium persulphate on cellulose.

Investigation showed 'activity' towards potassium iodide in terms of the following table :—

C.C. N/100 Iodine Liberated by 100 Grams of Active Cellulose.

Time of exposure to ozone.	Cotton.		Mercerised Cotton.		Viscose Silk.	
	Dry.	Air dry.	Dry.	Air dry.	Dry.	Air dry.
	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
7 hours	9	—	—	—	2·5	—
18 ,,	32	70	47	168	32	309

The value 70 for cotton represents 0·0056 per cent. of active oxygen ; that of 309 for viscose silk 0·025 per cent. Jute and beechwood showed no activity after exposure to ozone.

Properties of the Cellulose Peroxide :—

(*a*) On treatment with water hydrogen peroxide is slowly produced.

(*b*) Exposure to a temperature of 37° C. for 2 hours reduces the activity, while 2 hours at 95° prac ically destroys it.

(*c*) The activity persists for several weeks if the material is kept in a vacuum desiccator.

(*d*) The peroxide acts strongly on a photographic plate in the dark, giving images closely resembling those described by Russell (1904) in the case of the woods. With the 18 hours, air-dry products of the table above, good negatives were obtained in 20 days at 14° C., but at 37° similar negatives were obtained in 6 hours.

The active substance was volatile, the plates showing a band of reduced silver when fixed 5 mm. above the cellulose threads.

This photographic activity is no doubt due to nascent hydrogen peroxide, formed by the decomposition of the cellulose peroxide by water. Discussing the mode of attack of ozone the author considers that the peroxide oxygen attaches itself, possibly at a tertiary hydroxyl group, or more probably at a carbonyl grouping. The cellulose peroxide decomposes in the presence of water forming an aldehyde (oxycellulose), or it may act as a catalytic agent conditioning the further oxidation.

From the commencement of the ozone action, carbon dioxide is produced and acid develops in the cotton, the quantities of these (measured as $N/10$ alkali) being approximately equal as shown in the following table :—

ACTION OF OZONE (1·6 PER CENT.) ON BLEACHED COTTON CALCULATED TO 100 GRAMS OF DRY COTTON.

Time in hours	1	3	6	21
$N/10$ – NaOH c.c.	113	225	303	727
$N/10$ – CO_2 c.c.	176	258	341	—

The acidity could be removed either by neutralisation or by boiling with water. The residue (80 to 90 per cent.) showed

the properties of an oxycellulose, strongly reducing Fehling's solution, but not ammoniacal silver solution. It was shown to be very similar to an oxycellulose prepared by Tollens (1899), by the action of bromine water in neutral solution, but to differ from the products obtained with hydrogen peroxide (Bumcke). The constants of several of these preparations, after removal of the acidity, are given. Ozone exposure 24 hours: figures calculated to 100 of dry substance.

ACTION OF OZONE (2 PER CENT.) ON COTTON, MERCERISED COTTON, AND VISCOSE SILK.

	Cotton wool.		Mercerised cotton wool.		Mercerised yarn 2/60 gray (tension).		Viscose silk, 120 deniers.	
	Normal.	After 24 h. ozone.	Normal.	After 24 h. ozone.	Normal.	After 24 h. ozone.	Normal.	After 24 h. ozone.
Loss in weight	—	12	—	7	—	—	—	4·5
C. per cent. .	44·4	43·5	43·2	43·5	—	—	44·6	44·4
Methylene blue absorption .	0·3	2·1	0·4	3·1	—	2·3	1·6	1·8
Copper number	1·2	16·9	1·7	24·0	—	9·6	3·0	15·5
Loss in 10 per cent. KOH .	—	6 ‡	—	57	—	—	—	50

It will be noticed that the attack on the mercerised cotton wool, as evidenced by the high copper value, is very much greater than that on a yarn mercerised under tension. Viscose silk has a copper number intermediate between that of the mercerised yarn and the cotton, though not differing much from the latter. The breaking strengths show a similar agreement.

An exhaustive examination of the effect of 1·5 per cent. ozone on the bleaching and strength of textile fibres showed that, in general, but little loss of strength took place in one hour though the bleaching action was considerable. Before a

full bleach on cotton and linen could be obtained, however, a considerable weakening effect was produced.

Some cotton yarns and viscose silk showed an increase of strength during the first hour's exposure to moist ozone. Curves are given showing the variation of the breaking load with time, for each material.

The following table gives the time of reduction to one-half of the breaking strength, the threads being exposed to ozone of 1·5 per cent. concentration by weight :—

	Hours.
Grey cotton 2/60	12·5
,, ,, ,, (mercerised + tension) . .	22·0
Viscose silk (from wood cellulose) (120 deniers)	13·0
Flax, 65's	6·0
Natural silk, 16/1000	3·1

SOME EFFECTS OF THE ACTION OF ULTRA-VIOLET LIGHT ON COTTON FABRICS.

C. Dorée and J. W. W. Dyer (J. Soc. Dyers and Col., 1917, **33**, 17).

Few observations are on record with regard to the action of light on cellulose. In the presence of air and moisture Witz (1883), using the methylene blue test, claimed that oxycellulose was formed. Girard, however, asserted that it was more probably hydrocellulose. Witz (*ibid.*) also exposed a cotton fabric during a whole summer under conditions in which air and moisture were excluded, and found oxycellulose formation with the blue rays, but none with the yellow or red.

The rays from radium rapidly destroy the strength of paper (*Papierfabrikant,* 1907, **6,** 1349).

For the experiments recorded in this research a single-ply cotton fabric as used for airship envelopes was employed. It showed a very satisfactory purity as a cellulose. After exposure

for a week to the light from a Cooper-Hewitt mercury vapour lamp it had become of a biscuit-yellow colour and showed a complete loss of strength. When treated with 10 per cent. sodium hydroxide solution in the cold it gave the characteristic yellow colour associated with oxycellulose.

The following table contains the results of standard determinations made with the exposed fabric. For comparison, those of an oxycellulose prepared by the action of ozone (Dorée, 1912) are included :—

	Unexposed fabric.	Exposed fabric.	Oxycellulose made by the action of ozone.
Loss of weight in 1 per cent. boiling NaOH—			
5 minutes . . .	0·0	9·5	6·2
60 ,, . . .	1·0	13·6	15·5
Copper number . . .	0·62	4·0	8·0
Furfuraldehyde per cent. .	0·20	1·34	1·5
Methylene blue absorption per cent.	0·7	1·5	1·6

These very high values indicate a profound change in the material in the direction of oxycellulose formation. The ultra-violet light in the presence of air and moisture may not improbably act in two ways : there may be, first, some specific physical action of the rays themselves on the cellulose causing disintegration, and, secondly, there may in all likelihood be a development of ozone. It has been shown that ozone in the presence of water (the natural humidity of the cellulose being sufficient) acts strongly on the celluloses, converting them into acidic, alkali-soluble products having the properties of oxy-celluloses.

* * * * * * *

During the war the action of light on balloon and airship fabrics became of great practical importance. The following contribution carries the question a stage further :—

THE INFLUENCE OF ATMOSPHERIC EXPOSURE ON THE PROPERTIES OF TEXTILES.

A. J. TURNER (J. Soc. Dyers and Col., 1920, **36**, 165).

Linen fabrics exposed to weather were found to lose strength slowly in winter, rapidly in May, June and July. One exposed from March to August only retained 28 per cent. of its original strength. Curves are given showing that the deterioration is approximately exponential.

As light thus appeared to be the dominant factor in causing deterioration of fabric, an investigation was undertaken by F. W. Aston at the Royal Aircraft Establishment, with a view to determining if possible what parts of the visible or invisible spectrum were responsible for this deterioration.

The method adopted was to throw a spectrum of the mercury arc on a series of linen threads by means of a Hilger quartz spectrograph. The spectrum was photographed and the whole of the spectrum on the plate covered by a binding of threads laid close together, parallel to the spectrum lines. All except a half-inch of each of the threads was protected from the light by tin-foil. The negative was then replaced in the plate holder of the spectrograph and exposed exactly as an ordinary sensitive plate using the threads as sensitive surface.

Apart from loss of strength, another more sensitive criterion was available, viz. observation as to whether or not the thread broke at the part which had been exposed to light.

In a successful experiment, an exposure of 670 hours was given to a Westinghouse Cooper-Hewitt Quartz Mercury Arc, type Z. 2B, taking about 3 amperes at 200 volts; the image of the arc was projected on to the slit of the spectrograph by means of a short focus quartz lens : a very open slit was used giving lines covering about six threads. The total distance travelled by the light in the air was about 75 cms. The results obtained are shown in a figure in which columns represent lines

of the mercury spectrum, six threads wide. The intensities of the stronger lines are those determined by Ladenburg. A continuous curve shows the distribution of intensity in sunlight.

Conclusions.—(i) For wave-lengths greater than 3,660 A.U. there is no destructive effect. It is probably safe to conclude that visible light has little, if any, destructive effect.

(ii) There is apparently no limit to the action for shorter wave-lengths. This partly explains why direct light causes a loss of 20 per cent. per week, at 45 cms., while during four weeks the mean loss of strength over the whole spectrum was negligible.

(iii) The effect of a sheet of glass, which cuts off the spectrum below 3,990 A.U. is much greater for the mercury arc than for sunlight.

Although it is thus proved that light was necessary for deterioration in ordinary circumstances, the mode of action had still to be determined. As it has long been suspected that the action was through ozone, or hydrogen peroxide as intermediaries, experiments were made to elucidate the point. Preliminary experiments with strips of fabric showed that replacing air by hydrogen reduced the loss of strength from 20 to 6 per cent. Subsequently linen threads were used so that more tests could be made at the same time. These were wound on a strip of glass as before, and inserted in 15 mm. transparent quartz tubes. One tube was open at both ends so that air was free to circulate; the second contained phosphorus pentoxide at one end and was highly exhausted for a considerable time to dry the threads as far as possible; it was filled with dry air. The third was exhausted to a very high vacuum with repeated warming and then sealed off. The fourth was completely covered with tin-foil and was used as a control. The four tubes were placed under the mercury arc at a distance of 23 cms., and exposed for seventy-two hours. (The temperature rose to 59° C.) The results obtained were as follows:—

	Air (not dry).	Air (dry).	Vacuum.	Control.
Loss of strength per cent. .	34	34	10	—
Threads breaking on exposed				
part per cent. . . .	100	100	62	17

The conclusion drawn was that the removal of oxygen from the atmosphere surrounding the fibres very largely reduced but did not entirely eliminate the destructive action of the light ; the presence or absence of moisture seemed to be of no importance.

*   *   *   *   *   *   *

The results last recorded support the view that the ultra-violet rays have a specific action on cellulose in themselves, but that in presence of oxygen the effect is greater and of a definitely chemical character.   With regard to this last the formation and activity of ozone are indicated.   Lynam ('Spectroscopy of the Extreme Ultra-Violet') has shown that the light causing direct formation of O_3 from O_2 must have $\lambda < 1850$ A.U. and that it is completely absorbed by 1 mm. of air at ordinary pressure : no appreciable quantity of ozone can therefore be formed by the direct action of sunlight on air at the earth's surface.   It is difficult then to account for its formation in the linen threads above described.   Dr. F. A. Lindemann has worked out the following explanation :—

The most effective frequency ν for ionising a gas is given by $h\nu = e\bar{V}$, where h is Planck's constant, e the electronic charge, and $\bar{V}$ is the ionisation potential.   Taking this as 9 volts (Frank and Hertz) the frequency ν works out to give a wave-length $\lambda = 1380$, thus agreeing very well with the value 1350 given by Allen ('Photo-electricity,' p. 90).

But the energy required to move a charge e to infinity is of the form e^2/kr where k is the dielectric constant of the medium and r the radius of the molecule.   The most effective wave-length in a medium of dielectric constant k will be k times that in ozone itself, whose dielectric constant is nearly unity.   The

refractive index of linen was found to be approximately $1·53$, and since $k = \mu^2$ the dielectric constant of linen is $2·34$. This value gives for the region of the spectrum that should be most destructive, a wave-length $\lambda = 3230$ in good agreement with the observed results.

We now mention some contributions to the discussion of the nature of the equilibrium connoted by the term oxycellulose.

OXYCELLULOSE.

W. D. BANCROFT and R. H. CURRIE (J. Phys. Chem., 1915, **19**, 159).

The authors prepared a number of oxycelluloses by the usual methods and state that qualitatively they are similar substances whatever the method used. They all dissolve partially with a yellow colour in alkaline hydroxides and the residue is considered to be unchanged cellulose. The authors were never able to convert the whole of the cellulose to this soluble oxycellulose in one treatment and question whether 'pure' oxycellulose has ever been prepared. The α-oxycellulose of Nastjukoff (1901) is thus regarded as merely unchanged cellulose, the β- (alkali-soluble) and γ- (water-soluble) fractions are the same substance but in a different state of aggregation. The soluble products are regarded as the true oxycellulose and may be homogeneous.

The reducing property of oxycellulose may be accidental and due to the presence of products of decomposition. On prolonged heating this property disappears without any essential change in the other characters of the oxycelluloses.

These views receive confirmation in the following important paper in which a great volume of experimental data is collected:—

PURIFICATION OF CELLULOSES : THE ACTION OF ALKALINE EARTHS ON THEIR INCRUSTATIONS AND ON OXY- AND HYDROCELLULOSES.

C. G. SCHWALBE and E. BECKER (J. prakt. Chem., 1919, **100**, 19-47).

Action of Lime-water on Hydrocelluloses.—Tollens (1901) first showed that when boiled with lime-water hydrocellulose left, apparently, pure cellulose. In solution calcium isosaccharinate was found. The authors now ·confirm this, the copper numbers of the residue left after boiling with lime-water falling to those given by pure celluloses. Thus two hydrocellulose preparations with copper numbers 6·2 and 5·5 left residues with numbers 0·14 and 0 respectively. The views of Heuser and Herzfeld that hydrocellulose is composed of cellulose and dextrinous products of its hydrolysis, are in full agreement with these observations. The action of the lime-water is to break down the cellulose dextrin to isosaccharinic acid, leaving cellulose. The fact that purified cellulose is not attacked in any way by lime-water under the conditions employed (4 grams of cellulose, ·4 of lime and 100 of water, boiling 18 hours) was proved, since 100 of cotton cellulose gave 100·5 after 18 hours boiling. Extending the study of the action of lime-water to hydrocelluloses prepared from wood cellulose, the effect was again to lower the copper number from 8 or 10 to below 1, with a loss in weight of some 30 per cent. Calcium isosaccharinate was identified in this case also as a secondary product. Similar results were obtained with oxycelluloses of various origin. Soda celluloses are very slightly attacked by lime boil. ' Sulphite ' celluloses lose up to 50 per cent. of their pentosan content and their methyl number falls considerably. The residue still contains pentosan in extremely strong combination. The authors as the result of an exhaustive research conclude that—

Hydrocelluloses are mixtures of cellulose with decomposition products ; the so-called cellulose dextrins being present to the extent of 24 to 36 per cent.

Oxycellulose made by the action of bleaching powder consists of about 60 per cent. normal cellulose and 40 per cent. of associated oxidation products.

Sulphite cellulose contains dextrins similarly removable by lime-water.

The residue obtained in all these cases is a cellulose with practically no copper reducing power.

———— ————

We follow this interesting research with one in which criticism is directed against some of these conclusions :—

ARE HYDROCELLULOSES SIMPLE SUBSTANCES ?

H. Ost and R. Bretschneider (Zeit. angew. Chem., 1921, **34,** 422).

The authors seek to controvert the statements of Schwalbe and Becker that hydrocelluloses are mixtures of cellulose and cellulose dextrins.

They found that Girard's hydrocellulose (copper number 6·7) lost 24 per cent. of its weight on boiling with lime-water, but that the cellulose used (copper number 2), also lost 16 per cent. The residues showed, it is true, similar low copper numbers, namely 0·9 and 0·6 respectively, but the residue from hydrocellulose was essentially different from ordinary cellulose as shown by the viscosity of its solution in cuprammonium and the physical properties of its acetate.

*   *   *   *   *   *   *

As we have said these results cannot be accepted as conclusive. The cotton chosen as 'cellulose' with a copper

number of 2·0, represents a considerable degree of devia-
tion from a normal cellulose for which 0·5 would be a high
value.   Considerable attack by alkaline solutions might be
expected.   Viscosity determinations in cuprammonium solu-
tions also are, in the light of recent observations, only to be
relied upon under very special conditions of working which are
not mentioned in the paper.   Gibson (p. 110) has shown that
cuprammonium solutions of cellulose alter in viscosity to an
enormous extent on simple exposure to light or by shaking in
the presence of air.   Unless these facts were taken into account,
differences in viscosity have little value as proof of differences
between two cellulose products.

Coming more particularly to the action of acids, we note
that the exact nature of the attack of dilute solutions of acids
on cellulose has been discussed by Jentgen (*Zeit. angew. Chem.*,
1911, **24,** 11), and by Schwalbe (*ibid.*, p. 12).   The former
considers that, for example, in the formation of hydro-cellulose
by Girard's method, an adsorption compound between 'molec-
ular' sulphuric acid and cellulose is produced and that water
must be present, but not in sufficient quantity to cause complete
ionisation of the acid.   The adsorbed acid then promotes re-
action between cellulose and water, the acid acting as a catalyst,
with the formation of hydrocellulose.   Schwalbe on the other
hand contends that hydrolysis is the first effect even of the
weakest acid, and that this hydrolysis precedes esterification,
e.g. in the formation of acetates.   He has shown that Girard's
hydrocellulose can be formed by sulphuric acid of 0·001 per
cent. concentration which, when air-dried, would only have a
concentration of 0·02 per cent. in the fibre.   There is not
sufficient evidence available to decide between these views.
There is no doubt that the cellulose complex shows a marked
tendency towards resolution to the dextrose, or polydextrose,
configuration, and the very small quantities of acid which ad-
mittedly initiate this change probably enter into combination

at some point and condition the internal synthesis referred to above (see following papers). On this hypothesis it may well be that the initial change in the formation of oxy- and hydrocellulose is the same, viz. resolution to a complex based upon dextrose, this complex then undergoing oxidation or hydrolysis respectively.

The terms oxy- and hydro-cellulose should therefore be considered as denoting processes rather than chemical products.

THE ACTION OF DILUTE SULPHURIC ACID ON COTTON CELLULOSE, AND AN IMPROVED METHOD OF TESTING FOR OXYCELLULOSE.

E. Knecht and F. P. Thompson (J. Soc. Dyers and Col., 1921, **37**, 270).

After referring to the previous researches of Girard (*C.R.*, 1875, **81**, 1105), H. Koechlin (*J. Soc. Dyers and Col.*, 1888, 163), and W. Harrison (*ibid.*, 1912, **28**, 238, 359), the authors describe the effects of treating cotton cellulose with an equal weight of dilute sulphuric acid (5 to 10 per cent. H_2SO_4) and drying at low temperatures (40 to 50° C.). The changes observed and measured; loss of strength (yarns), increased copper (CuO) reduction (Felhing), and affinity for specific colouring matters, are compared with those determined by HCl . Aq, and an oxidation to 'oxycellulose' by Mn_2O_7 ($KMnO_4$ in dilute H_2SO_4). This latter product, representing the effect of a fractional proportion of oxidising oxygen (O : 12 . $C_6H_{10}O_5$), was identical with the two 'hydrocelluloses' in regard to CuO reduction; whereas in regard to fixation of colouring matters the 'oxycellulose' was similar to the product of action of H_2SO_4 . Aq, both being differentiated from the product of action of HCl . Aq. On further investigation it was found that the former 'hydrocellulose' contained 'fixed sulphur' which was estimated.

The results show that 'when dilute sulphuric acid is dried into cotton, the cellulose is hydrolysed and tendered, and fixes some of the acid (0·97 to 1·14 per cent. under the conditions described) which acts as a mordant for basic colours.'

The authors also point out that 'the characteristic affinity of Chardonnet "silk" for basic colours is due to the sulphur (or sulphuric acid) fixed during the nitration with mixed acids, and not during denitration.'

*   *   *   *   *   *   *

The interest of this investigation is that of a limiting case of the relationship of H_2SO_4 to cellulose, and the results would have gained in significance by weighing the cellulose after 'drying' (40 to 50° C.) from the diluted acid which would have determined the concentration of the acid in the fibre. This probably did not exceed $H_2SO_4 . 3H_2O$. The fixation of SO_4H, as an ester hydrate, confirms and extends the observations of M. Cunningham (loc. cit.). The resistance of the ester group to alkaline saponification confirms the observations of Cross and Briggs on the SO_4H groups of the aceto-sulphates (*Ber.*, 1905, **38**, 1859). The presence of SO_4H residues in collodion 'silks,' surviving alkaline denitration, follows from the above in connection with the investigations of the 'nitration' process (Cross, Bevan and Jenks, *Ber.*, 1901, **34**, 2496).

A continued investigation would further differentiate between the three factors of the complex effect ; structural break-down of the fibre, formation of free aldehydic groups, and fixation of SO_4H ; and might definitely localise the ester reaction in a particular component group.

CELLULOSE OXALIC ACID ESTER.

J. F. BRIGGS (J. Soc. Chim. Ind., 1912, **31**, 520).

Bleached linen cloths on which oxalic acid solution had been accidentally spilled were found, after storage for a year

at ordinary temperature, to be converted into a friable hydro-cellulose. In one case, although the product was acid, no acid of any kind could be extracted by water. The cellulose had therefore become converted into an insoluble acid with properties which might be expected in the case of the acid cellulose ester of a dibasic acid.

Oxalic acid in the presence of dextrin on the other hand was found by Knecht to give no oxalic ester and the material was not tendered.

In order to investigate the conditions of formation of this ester the author steeped purified cotton in solutions of oxalic acid of varying strengths. After squeezing and drying the pieces were heated at 45° to 50° C. for thirty hours. The oxalic acid combining was estimated against a control piece (i) by extraction with water, and (ii) by treatment with sodium acetate solution, drying and incinerating, with subsequent estimation of the alkalinity of the ash. The results obtained were as follows :—

Concentration of the oxalic acid per cent.	Temperature (Centigrade).	$C_2H_2O_4 . 2H_2O$ combined per cent. on the cellulose.
5	45 to 50°	1·0
10	45 to 50°	2·3
10	95°	3·7

To ascertain the maximum effect the cotton was plunged into fused oxalic acid, removed and heated at 95° C. for four days, by which time the crust of acid had volatilised. In this case 6·4 per cent. of acid was fixed.

These experiments show that oxalic acid when heated in the dry state with cellulose at moderate temperature combines with it in small proportions. The ester shows a tendency to hydrolyse during washing although the sodium salt is stable. It has a strong affinity for basic dye-stuffs.

     *   *   *   *   *   *   *

The next group of papers to be noted deals with the action of minimal quantities of acid, important alike from a theoretical and a technical standpoint :—

THE ACTION OF MINERAL ACIDS ON COTTON.

M. COHEN (J. Soc. Dyers and Col., 1915, **31**, 162).

The author determines the minimum concentration of acid which can be said to have an effect on cotton, by measurements of the copper number by Schwalbe's process. His method and results are summarised in the following tables in which we have rounded off some of the values obtained. In the series of experiments in which the cotton was soaked in cold acid, no indication is given of the weight of acid retained by the fibre before drying at 120°.

I. Action of acids of varying concentration on cotton.

| | Copper number of cotton which has been | | | |
| | (a) | (b) | (c) | |
Strength of acid per cent.	Boiled in HCl 1 hr.	Boiled in H_2SO_4 1 hr.	Soaked in cold acid, dried at 120° C. for ten minutes. HCl	H_2SO_4
1·0	3·3	2·54	—	—
·5	2·2	1·82	—	—
·25	1·6	1·33	—	—
·125	1·2	1·00	—	1·32
·067	0·9	0·77	—	0·99
·033	0·8	0·61	—	0·80
·016	0·65	same as	—	0·66
·010	—	distilled	0·90	—
·008	0·60	water	—	0·57
·007	same as	,,	0·76	—
·005	distilled	,,	0·66	—
·002	water	,,	0·57	—
Aq. dist.	0·54	0·54	0·53	0·53

II. Table showing the relationship between the copper number and the tensile strengths of cotton yarns after boiling with sulphuric acid for one hour.

Concentration of acid per cent.	1	·5	·25	·125	·067	·033	·000
Tensile strength	220	340	390	440	495	535	575
Copper number .	2·5	1·8	1·3	1·0	0·77	0·61	0·84

THE ACID 'TENDERING' OF COTTON CLOTH.

J. H. LESTER (J. Soc. Chem. Ind., 1915, **34,** 934).

In this note the author points out the variability in the effects observed in the action of traces of acid under various technical treatments, e.g. 'the strength of a cloth containing 0·35 per cent. of hydrochloric acid dropped from 82 to 65 lbs. when dried in air at 25° C., yet a sample containing only ·05 per cent. of acid lost practically the whole of its strength when completely dried under a hot iron.' The hot iron test he regards as of greater practical value than direct estimations of acidity. In his experiments the cloth was treated with ·01 and ·1 per cent. respectively of its weight of hydrochloric acid. Each was dried (*a*) under a hot iron, (*b*) under the iron, followed by 1½ hours in water-oven.

		Blank.	·01 per cent. HCl.	·1 per cent. HCl.
Breaking strain under $\{$	(*a*)	105	100	90
	(*b*)	95	92	13

The author concludes that the limit of acid allowable in cotton cloth is ·01 per cent. of its weight of free hydrochloric acid. He considers that the tendering effect of acids upon cotton may be regarded as mainly dependent upon (*a*) the concentration of the acid referred to the total moisture in the cotton, e.g. if a sample contains ·1 per cent. of acid and in the air-dry state contains 8 per cent. of moisture, the concentration of the acid solution will be 1·25 per cent., and (*b*) the temperature and time to which the cotton is exposed while the content of moisture is unchanged.

     *   *   *   *   *   *   *

In extension and criticism of these contributions we refer to a paper on 'The Detection and Estimation of Acidity and Alkalinity in Cotton Fabrics,' by G. M. Wigley and Dr. H. F. Coward of the Tootal Broadhurst, Lee Co., Ltd., Research

Department. We are indebted to the authors for an advance proof of this paper (*J. Textile Inst.*, 1922), the substance of which is as follows :—

Spotting tests have long been used for qualitative purposes to examine the reaction of a fabric, without any inquiry into their efficiency. The Brit. Eng. Standards Association specify that the acidity or alkalinity of an aeroplane fabric shall be estimated by titration of an aqueous extract in absence of the fabric.

Two fabrics were steeped in acid and alkali respectively and extracted repeatedly with hot water. Methyl red was the only indicator which showed any difference between them, and it was proved that a fabric which gives a neutral reaction with methyl red contains less than ·005 per cent. acid or alkali respectively. Salt solution removed acid more quickly than pure water.

Using the B.E.S.A method (two extractions with boiling water, titration with N/100 NaOH) it was found that with 0·01 per cent. H_2SO_4 on the weight of the cloth, the acid remained in the cloth and at 0·1 to 0·2 per cent. acid only one-half was removed. The method of titration directly in presence of the cloth, using phenolphthalein and N/50 alkali, showed that with cotton containing ·008 to ·033 gram H_2SO_4 per 100 grams cotton, the error of estimation was of the order of + ·005 gram ; from ·06 to ·26 of the order of only − ·003 gram ; using brom. thymol blue the error throughout was ± ·005. Neutral salts did not interfere.

Methyl red is recommended for spotting tests, giving bright red on a cloth containing ·005 per cent. acid, yellow at ·005 per cent. alkali ; lacmoid gives a red ring with a blue centre with cloth of acidity 0·03 to 0·06 per cent. ; methyl orange indicates only at 0·1 per cent. H_2SO_4. Phenolphthalein gives no colour with a fabric containing sodium carbonate till the amount reaches the equivalent of 0·12 NaOH on the weight of cloth.

THE TENDERING OF COTTON BY ACIDS AND SALTS.

M. Fort and F. Pickles (J. Soc. Dyers and Col., 1915, **31**, 255-260).

Discussing the inhibiting action of Glauber's salt on the tendering of cotton by dibasic organic acids, the authors say that 'the clear views obtained from electro-conductivity experiments with solutions of acids and salts render it desirable that where the tendering of cotton is due to the presence of the latter these views should be applied if possible.'

Experiments were first made with acids of definite normality on 5 grams of cotton yarn under a reflux at water-bath temperature. The following table shows the 'strength' of the acid as measured by its relative conductivity and the percentage loss of strength of the cotton—the two running roughly parallel :—

	Normal Solutions.				
	HCl	H_2SO_4	Oxalic	Acetic	$NaHSO_4$
Acid					
Relative conductivity . .	100	65	19·7	0·4	—
Per cent. loss of strength .	100	93·3	71·1	10·9	53

	Double-normal Solutions.					
	Oxalic	H_3PO_4	Chlor-acetic	Tartaric	Formic	Acetic	Water
Acid . .							
Relative conductivity .	19·7	7·3	4·9	2·3	1·7	0·4	—
Per cent. loss of strength	72·7	36·8	42·0	34·4	19·7	17·1	4·5

The papers which follow deal more especially with the nature of the hydrocellulose equilibrium :—

ACTION OF DILUTE MINERAL ACIDS ON CELLULOSE.

A. WOHL and K. BLUMRICH (Zeit. angew. Chem., 1921, **34**, 17).

Basing a theory upon some earlier work on the action of acids on carbohydrates (*Ber.*, 1890, **23**, 2097), the products of the hydrolysis of cellulose are stated to be able to react with the residual cellulose in its colloid phase. As the copper number shows, there are also liberated in the residues, through the elimination of sugar molecules as the result of hydrolysis, aldehyde or half-acetal groups, and these groups enter into acetal formation with the free (OH) groups of the cellulose residue; the reaction being more complete than in solution because of the very high concentration of carbohydrate in the colloid phase. This explains why the residual hydrocellulose does not possess the properties of an intermediate product (e.g. insoluble dextrin) but rather those of the insoluble 'reversion dextrins' (loc. cit.) It also makes clear the well-known fact that hydrocelluloses on repeated hydrolysis appear to be less easily attacked than the original cellulose and are of no use for feeding purposes.

The following results were obtained by heating cellulose, with a copper number of 1·2 (uncorr.), on the water bath with dilute hydrochloric acid for varying periods.

Grams of copper reduced per 100 grams dry cellulose : (*a*) in residue, (*b*) in solution :—

Time (hours)		·25	1	2	4	6	12	20
HCl 0·5 per cent.	(*a*)	2·3	4·1	4·6	—	5·5	6·3	6·7
	(*b*)	—	—	1·5	—	2·8	5·0	9·5
HCl 3 per cent.	(*a*)	—	5·5	5·9	5·5	5·3	5·3	5·7
	(*b*)	—	3·1	6·8	9·5	10·9	15·0	13·9

These results show that on slow hydrolysis cellulose, like starch, not only splits off glucose molecules, but also carbohydrates of

higher molecular weight which then undergo further resolution in solution.

HYDROCELLULOSE.

O. Heuser and H. Herzfeld (Chem. Zeit., 1915, **39**, 689).

Analyses of hydrocellulose preparations vary within wide limits rendering it unlikely that hydrocellulose can be considered as a homogeneous substance. The authors confirm this opinion by some experiments on the following lines: Girard's hydrocellulose was extracted with boiling water in a Soxhlet apparatus and the copper number of the residue determined at intervals of 12 hours. The value of this constant decreased, at first quickly and afterwards very slowly, from 5·4 to 0·8 after nearly 4 days' extraction, the value being 2·0 at the end of 1½ days and 1·0 after 2½ days. The residue was now again converted to hydrocellulose by Girard's process and the new product (copper number 4·0) again extracted. After 3 days the value had fallen to 0·8 as before.

The curves showing the rate of decrease of the copper number had the same form, reversed, as a curve representing the formation of an adsorption compound with a gel. It is therefore suggested that hydrocellulose is an adsorption compound of variable composition consisting of cellulose in combination with its products of hydrolysis, including dextrose, and most probably various dextrins, the brittle nature of the product being partly attributed to the interpenetration of the cellulose structure by gelatinised products of hydrolysis.

*   *   *   *   *   *   *

The conclusions of the authors appear to be on a sound basis and their method of experiment is simple and definite. The intermediate products of hydrolysis included under the term cellulose dextrins, though of technical importance, have

been but little studied from a scientific point of view and we therefore mention at this point an investigation of recent date.

SOME CELLULOSE DEXTRINS.

M. SAMEC and J. MATULA (Koll. Chem. Beihefte, 1919, **11**, 37-73).

This paper constitutes an exhaustive study of the action (*a*) of sulphuric acid of 50 to 85 per cent. concentration at 20° C., and (*b*) of phosphoric acid of 76 to 85 per cent. concentration at temperatures ranging from 50 to 70° C. on a sulphite cellulose ; the reaction periods varying up to six days.

The progress of the degradation of the cellulose is followed (1) by the variation in the colours given by iodine, viz. change of the blue to violet, violet to brown and disappearance of colour.

(2) Variation in the proportion of water-soluble products.

(3) Effect of precipitation by alcohol.   Under this head the authors state that dextrin esters are first formed and that on addition of more alcohol the following conditions may arise : (*a*) the esters may gelatinise after which dextrin precipitates ; (*b*) both the dextrins and their esters may be insoluble in alcohol ; (*c*) the former may be insoluble, the latter soluble in alcohol ; (*d*) both may be soluble.

(4) By observations of viscosity, optical rotation, and solubility in 10 per cent. sodium hydroxide.

With sulphuric acid of strengths above 85 per cent. charring occurs.   With acid concentration varying from 85 to 75 per cent. after thirty minutes, products are obtained completely alcohol-soluble.   On heating the solution, the esters are decomposed, and a thick white precipitate of dextrin is formed. Acids between 75 and 65 per cent. yield products which, on addition of alcohol, give a stiff transparent jelly.   Boiled with excess of alcohol this gives a white flocculent mass.

With phosphoric acid of concentrations higher than 75 per cent., a colourless viscous jelly is formed, but the attack of this acid differs markedly from that of sulphuric acid, the degradation of the cellulose being very slow: thus with acid of 85 per cent. concentration at 50° the blue colour at first given by iodine only changes to violet at the end of sixteen hours. Water-soluble products are observed at the end of forty-six hours, whereas these are found after one hour with sulphuric acid of 60 per cent. concentration.   These cellulose phosphoric acid jellies are highly viscous, which indicates a very complete esterification of the dextrins produced.

Five typical dextrins of various solubilities and properties were particularly obtained and described.   The results show that their properties vary not only with the concentration of the acid, but with the relative mass of cellulose and acid employed.

     *   *   *   *   *   *   *

This communication continues the work of Schwalbe and Schulz on 'Intermediate Products of the Hydrolysis of Cotton Cellulose by means of Sulphuric Acid' (*Zeit. angew. Chem.*, 1913, **26**, 499), in which details of preparation, colloidal properties, the alkali solubility, the copper value and other characteristics of a number of well-known modifications were described.   These included Guignet's cellulose, Flechsig's amyloid, Ekströms acid cellulose and parchmentised cellulose.

———

Many tests have been described purporting to distinguish between oxy- and hydrocellulose, but none are very definite. Justin-Mueller (*Bull. Soc. Chim.*, 1921, [iv.], **29**, 987) states that if submitted to a dry heat hydrocellulose turns brown at 130 to 150°, at which temperature oxycellulose shows at most a pale yellow and cellulose is uneffected.   On the quantitative side the reducing value of these substances is an important constant for which reason we note :—

AN ACCELERATED METHOD OF ESTIMATING THE REDUCING VALUES OF CELLULOSIC SUB-STANCES.

E. KNECHT and L. THOMPSON (J. Soc. Dyers and Col., 1920, **36**, 254).

Since all forms of cellulose absorb copper from Fehling's solution a correction is necessary in carrying out the standard determination of the copper number by Schwalbe's method (*Zeit. angew. Chem.*, 1917, 121). This correction (the hydrate copper number) has perforce to be determined in the cold, an uncertainty being thereby introduced.

The authors give two methods, for details of which the original should be consulted, by which this uncertainty may be overcome and considerable time saved in the analysis.

In the first the reduction is carried out as in the original Schwalbe method. To estimate the copper reduced, however, the cuprous oxide is dissolved in an acidified solution of iron alum and the equivalent of ferrous iron produced estimated by titration with permanganate (Sutton, 'Volumetric Analysis,' 9th ed., p. 186).

The result may be confirmed by estimating the copper in the filtrate by means of titanous chloride. This gives, by difference, a result which includes the hydrate copper value.

The second method depends upon the precipitation of cuprous thiocyanate by oxycellulose from a solution of copper sulphate and potassium thiocyanate; sodium carbonate and citrate must also be present. The precipitate is digested with sodium hydroxide and the cuprous oxide produced is treated with iron alum and the copper estimated as before. The results obtained are slightly higher than with Fehling's solution.

Since no method of estimating the reducing value of oxy-cellulose other than by the reduction of copper has previously been employed, the authors reduced rosinduline G in alkaline

solution with their oxycellulose, estimating the unreduced dye-stuff by means of titanous chloride. A value of 13·3 (calculated as Cu) was obtained instead of 14·2 by Schwalbe's process.

'HYDROCELLULOSE' AND 'OXYCELLULOSE.'

The review of the literature embodying this latter research work, with respect also to the anterior position of the subject which it seeks to develop, leads to a critical and inevitable conclusion—that there are no lines of demarcation or differentiation justifying the terms hydro- and oxy-cellulose as applied to chemical individuals. The terms rather connote reactions, and the products represent phases of equilibrium of complex effects, in part determined by the reagent and conditions of action, in part the result of rearrangements, through the weakening or liberation of internal strains. When a normal cellulose is attacked by acids or by oxidants the actions are progressive, but the effects are not proportionate to the quantity (or concentration) of the reagent. By contrast, the interactions of cellulose with alkalis are graduated in relation to the active reagent over wide ranges of variation.

The products from the former actions are very obviously mixtures and readily fractionated by treatments calculated to determine the minimum of further change ; whereas the treatments of cellulose by alkalis, considered generally, do not affect the fundamental characteristic of the complex, viz. that of reaction as a homogeneous body or system. The contrast is of first importance, and the interpretation is an objective which demands a careful review of the whole subject of the degradation of cellulose under the action of reagents which have this obvious tendency or effect ; obvious by reason of the sensible changes of visible structure, or of structural properties which mark even the earliest stages of the action.

The entire technology of 'cellulose' rests upon this contrast, long recognised and empirically defined.   The literature of 'hydrocellulose and oxycellulose' is co-ordinate with this empirical conception of properties and processes, and a critical estimate of the research work embodied in these records leads to the conclusion that it has contributed little to the elucidation of the more fundamental problems of constitution.

The definite progress from this state of knowledge in the particular section under review is to be sought in the application of theoretical conceptions—in other words, generalisations from the entire range of the researches which have advanced our knowledge of 'cellulose' to its present position.

It is not necessary to repeat ourselves by formulating a series of working hypothesis which would shape investigations for the particular elucidation of the subject of this section. They should, they must be, obvious to the student.   All we insist upon is a critical preliminary study of the literature as necessary for disposing of a mass of complications, with some unrealities, which are in part due to the misleading terminology formerly adopted, but now out of date.

CHAPTER VI

LIGNOCELLULOSES AND LIGNONE

THE direction of investigation in this section during recent years has obviously followed the industrial importance pertaining to some of the woods, the nature and quality of the celluloses obtainable from them, together with the problem of the composition and mode of union of the characteristic component denoted by the term lignin or lignone.

At the same time, in dealing with such products it is necessary to keep in mind that wood is not only an organised structure, but also a complex representing an equilibruim, extraordinarily stable towards water and oxidation under natural conditions, yet obviously unstable in relation, more especially, to oxygen, of which it is, under special circumstances, remarkably greedy, and to micro-organisms : the latter being apparently able to bring about radical changes in both directions, degrading the cellulose components even to water-soluble products, and, alternatively, producing an up-grade change of the hydrobenzene groups to definitely aromatic compounds.

The woods, such as spruce and beech-wood, which have recently been studied very closely do not, for these reasons, constitute a suitable medium for the elucidation of the chemistry and the genetic relationships of fundamental component groups. From this point of view the simple lignocelluloses, typified by the annual jute, form a much more promising, although generally neglected, starting-point.

Again, the physiology of the wood fibre might be largely developed by a study of types specially selected to give the greatest amount of information. Many woody-structures contain secretions of definite constitution as, for example, the hæmatoxylin of logwood, and these may well be related in the plant metabolism to the lignocellulose mass in which they occur—physiologically they may be down-grade products; chemically we regard them perhaps as up-grade; but their investigation from this point of view would be highly productive. As an example we note briefly a contribution which illustrates our meaning :—

SAL BARK (*SHOREA ROBUSTA*) AND SOME PHYSIOLOGICAL PROBLEMS.

C. F. Cross and E. J. Bevan (J. Soc. Dyers and Col., 1919, **35,** 68).

The *Shorea Robusta* is the most important forest tree of the Himalayas, forming a dense wood (sp. cr. 0·9) and a fibrous bark which is used in the Indian tanning industry. Average specimens showed the following characteristic features of composition :—

Moisture . . . 7·6 to 8·8 per cent.

Mineral matter (ash) 8·5 to 9·8 ,,   Mainly (ash) $CaCO_3$ derived from CaC_2O_4.

Water soluble . 20·7 to 23·4 ,,

Tannins by hide powder test, 10·5 to 12·6 per cent.
Non-tans, 10·2 to 10·8 per cent.

The ash was found to be due to the secretion of calcium oxalate in unusually high proportion, 8 to 10 per cent. CaC_2O_4.

On these figures is based an industrial process of utilisation, comprising (1) exhaustion of water soluble and concentration to tanning extract; (2) exhaustion of residue by hydrochloric acid, separating the calcium oxalate and recovering the HCl (excess); (3) reducing the residue by alkaline digestions to a 'pulp' (yield 42 per cent.) to be utilised in the manufacture of boards and wrapping papers (U.K. Patent, 1917).

The bark is interesting as a physiological type from the unusual proportion of oxalate. As a product of respiration oxidation, oxalic acid is formed in high proportion by the *Aspergillus Niger*, from a varied range of nutrients, carbohydrates, oils, peptones, glycerin, and hydroxy-acids (tartaric). The problem presented by Sal bark is to localise the processes of oxidation obviously involved and to determine whether related to the secondary changes of lignification or cuticularisation. The problem is discussed from the point of view of recent contributions to these subjects (*ibid*, 1916, **32,** 1919, **35, 70**).

*   *   *   *   *   *   *

The first group of papers to be noted proposes and attempts to answer the following questions : ' Is there one cellulose only, viz. cotton cellulose, and therefore is the furfuroid found in wood, cereal, esparto, and other " celluloses " an " impurity ? " If this furfuroid be removed by repeated alkali extraction, is the cellulose left identical with cotton cellulose ? ' To the chemists responsible we would say that they appear to be under the influence of a definition of cellulose which is entirely arbitrary. It is true that we must be satisfied with an empirical definition, but it is one which is capable of very close statement. Cellulose is an integral residue from a mixture which has been treated by processes specifically selected to attack and afterwards dissolve component groups—the treatments being devised to produce the minimum of incidental modification.

In our view it is quite arbitrary to refuse the definition of cellulose to a complex containing furfural-yielding groups in any proportion. 'Extraction' with alkali is not intelligible to us except to obtain a particular fraction of the cellulose free from pentosan. We note, too, that 'separation' of component parts by 'extraction' is too lightly regarded as giving by integration an exact picture of the parent structure or complex. Extraction processes are rightly so-called in the case of a solvent of neutral character, but a resolution which involves attack by chemical agents cannot in any sense be regarded as a mere extraction. The necessity for keeping these criticisms in mind will become obvious as the reader proceeds.

WOOD CELLULOSE.

E. HEUSER and B. BOEDEKER (Zeit. angew. Chem., 1921, **34,** 461).

The authors maintain that plant cellulose from whatever source derived is a chemical individual and that there is only one cellulose, namely, that represented by the formula $(C_6H_{10}O_5)_n$. They regard the furfural usually obtained from purified celluloses as extraneous and do not agree with the view of Cross and Bevan and of Schwalbe, that the origin of this furfural is not a pentosan grouping, or that, if it is, it is a pentosan chemically combined as part of the cellulose complex.

Previous work (Heuser and Haug, *Zeit. angew. Chem.*, 1918, **31,** 99) showed that straw cellulose after repeated extraction with caustic alkalies followed by mild acid hydrolysis, is identical with cotton cellulose, giving no furfural on distillation with hydrochloric acid. In the present paper the similar identity of wood cellulose, after removal of pentosans, etc., is demonstrated. For this purpose a bleached sulphite cellulose was used and purified by two methods : (*a*) by boiling three

times with sodium hydroxide solution of 6 per cent. concentration; (*b*) treated three times with cold 17 per cent. sodium hydroxide solution.   The results were as follows in percentages on the original dry wood :—

Treatment.	Ash.	Moisture.	Pentosan.	Cu number (corr.).	Pentosan in solution.	Yield of pure cellulose.
Original . . .	0·5	7·2	4·06	4·1	—	—
(*a*) 6 per cent. NaOH	0·4	4·0	1·9⅓	0·9	0·12	85·0
(*b*) 17 ,, ,,	0·2	3·8	1·81	0·8	2·26	90·0

In order further to confirm the identity of these celluloses with cotton cellulose they were converted into glucose by the method of Willstätter (HClAq).   The formation of glucose as shown by cupric reduction and polarimeter ran parallel to that with cotton cellulose.   Finally, crystalline dextrose was isolated in a yield of 94 per cent. by following the procedure of Ost and Wilkening.

*   *   *   *   *   *   *

We can only repeat that by the isolation from sulphite cellulose of a product which still shows a pentosan content of 1·8 per cent. and a copper value of 0·8, the term pure cellulose in one sense may be justified, but it by no means establishes the identity of this product with cotton cellulose—nor is this proof necessary.

We next mention a paper containing a critical examination of similar purified celluloses from wood cellulose.   The authors rightly restrict the term pentosan to the complex yielding definitely furfural, as evidenced by the formation of a precipitate with phloroglucinol insoluble in alcohol (see also p. 149).

RESEARCHES ON WOOD CELLULOSE.

F. Lenze, B. Pleus and J. Müller, (J. prakt. Chem., 1920, **101**, 213-264).

The question of using wood cellulose for explosive manufacture led to a critical examination of the ' a-celluloses ' isolated from soda and sulphite cellulose respectively, by the action of five times the weight of 17·5 per cent. sodium hydroxide ('Researches,' III., 1905-10, p. 22). With cotton, after an initial loss of some 5 per cent., repeated extractions continued to remove about 0·6 per cent. in each case. The alkaline solution of the first extraction alone, gave a small amount of furfural phloroglucide compound on distillation with hydrochloric acid. The soda cellulose lost on repeated treatment with the mercerising soda 20, 10, 4, 2, 1·5 per cent., the subsequent extractions removing constantly about 0·8 per cent. The first two extracts only, gave pentosan (phloroglucide insoluble in alcohol).

Using ten parts by weight of alkali to one part of cellulose, the alkali-soluble pentosan was removed in one extraction. Sulphite cellulose showed similar results. Of the a-celluloses that from cotton alone gave a phloroglucide soluble in 80 per cent. alcohol, indicating that the others contained xylose complexes more firmly fixed than those dissolved by the alkali, though the amount in each case was less than 1 per cent. of pentosan.

A critical examination of the β- and γ-celluloses shows that these do not, as formerly thought, consist of oxy- and hemicelluloses respectively, but that they are mixtures. Two sulphite celluloses examined, gave β-celluloses containing 43 and 65 per cent. respectively of oxycellulose and smaller amounts of hemicellulose. The two γ-celluloses gave 13 and 21 per cent. of oxycellulose and large quantities of hemicellulose.

The authors, therefore, deal with the alkali-soluble celluloses as a whole and state that on hydrolysis, xylose and mannose result in the first instance and then glucose. For the estimation of mannose, boiling for five hours with 4 per cent. hydrochloric acid solution, followed by precipitation with *p*-bromophenylhydrazine, gave the best result. Full details of the method are given.

The oxycellulose which the authors regard as contained in all wood celluloses, is dissolved by the 17 per cent. alkali. An exhaustive investigation showed that this could be estimated by heating the neutralised liquors for three hours with 5 per cent. nitric acid, which dissolves the hemicelluloses, precipitating the oxycellulose unchanged. The details are given and the method is strongly recommended in preference to the copper number, or Vieweg's acid number, which are shown to bear no relation to the values obtained by the new method or to one another.

*   *   *   *   *   *   *

This paper contains a wealth of analytical detail. The assumption of pentosan-free cellulose identical with cotton cellulose is founded on the view of cellulose as a chemical individual represented by a definite formula. To cite the extreme case the furfural-yielding components of espartocellulose represent 30 per cent. by weight of the complex, which, however, ranks with cotton substance as a typical cellulose.

The authors state that only phloroglucide precipitates insoluble in alcohol are to be regarded as indicating pentosan complexes. They refer to the *brown* precipitates obtained, which differ from those of methylfurfural-phloroglucide derived from xylose. These can be explained in the light of the following research as due to hydroxymethyl-furfural derived from hexosan groupings.

THE PRODUCTION OF ω-HYDROXY-s-METHYL-FUR-FURALDEHYDE FROM CARBOHYDRATES AND ITS INFLUENCE ON THE ESTIMATION OF PENTOSANS AND METHYLPENTOSANS.

M. CUNNINGHAM and C. DORÉE (Biochem. J., 1914, **8**, 438).

Referring to the Kröber method for the estimation of fur-fural as the phloroglucide, the authors refer to a number of cases cited in the literature in which distillates have been obtained which gave a red or brown precipitate with phloro-glucinol although no pentosan or methylpentosan was present in the original substance. The precipitate given by methyl-furfural is soluble in alcohol, and at the present time it is customary to regard the alcohol-soluble portion of the precipitate as representing methylpentosan. In the present paper the authors claim that there is no real justification for this, and that the (alcohol-soluble) precipitates noted above, together with the alcohol-soluble portion of those given by substances undoubtedly containing pentosans such as the woods, are compounds of ω-hydroxymethyl-furfuraldehyde derived from *hexosan* group-ings.

Since methyl-furfural does not give the pink colour with aniline acetate, it is customary to use a solution of aniline in alcohol as an indicator for this aldehyde. The authors found that the rose colour given by aniline-alcohol persisted in por-tions of the various distillates (described in the table below), long after the aniline acetate paper had ceased to indicate the pre-sence of furfural. Thus with 2 grams of jute (yielding furfural 9 per cent.) 210 c.c. of distillate were obtained before the aniline acetate test failed—practically the whole of the phloro-glucide given by this distillate was insoluble in alcohol, indicating that furfural alone was present. But on continuing the distill-ation and using aniline-alcohol as indicator, 950 c.c. more were distilled over before this reagent ceased to give a rose colour.

Van Ekenstein and Blanksma (*Ber.*, 1910, **43,** 2355) have shown that hexose groupings readily yield ω-hydroxymethyl-furfuraldehyde on treatment with dilute acids, and that many of the colour reactions given by hexoses are due to this alde-hyde. In order to support their opinion that this hydroxy derivative is present in many of the Kröber distillates, the present authors prepared pure specimens of the aldehydes and give the following table :—

THE REACTIONS OF FURFURALDEHYDE AND ITS DERIVATIVES.

	Furfuralde-hyde.	Methyl-furfuraldehyde.	ω-Hydroxymethyl-furfuraldehyde.
1. Aniline-acetate . .	pink	yellow	pink
2. Aniline-alcohol . .	bright red	yellow-red	bright red
3. Phloroglucinol-ppt. .	black	red	red-brown
4. „ -filtrate	green	red-brown	orange-red
5. Absorption spectrum of (4) . . .	none	band in blue-green	band in blue-green
6. α·Naphthol + H_2SO_4*	grey red greenish	colourless scarlet greenish	violet crimson emerald-green
7. Thymol in alcohol + H_2SO_4 . .	red, violet above	red-pink, yellow above	scarlet with violet above
8. Barbituric acid . .	yellow ppt.	yellow ppt.	no ppt.

* Colours given in order from the top.

The second portion of the distillates from all the substances mentioned in the next table gave reactions indistinguishable from those shown by ω-hydroxymethyl-furfuraldehyde.

Analysis indicated a formula $C_{12}H_{10}O_5$ for the phloroglucide of the hydroxymethyl-furfural, giving a factor 0·54 for conver-sion of the weight of precipitate obtained to hydroxymethyl-furfural, and a substance giving all the reactions of this alde-hyde was isolated from the hydrolytic products of viscose silk. Some of the results obtained with various materials are quoted here :—

Substance.	Weight (anhydrous).	Distillate c.c.*		Weight of phloroglucide.	Weight soluble in alcohol.	Furfuraldehyde per cent.	ω-hydroxy-methyl-furfuraldehyde per cent.
1. Dextrose . .	2·123		610	0·0565	0·0550	0·18	1·6
2. Lævulose . .	3·770		240	0·0843	0·0712	0·20	1·1
3. Starch (potato) .	3·774		680	0·0981	0·0902	0·15	1·4
4. Cellulose (cotton wool) . .	2·021 {	(a)	100	0·0073	none	0·20	—
		(b)	600	0·0344	0·0115	(0·67)	0·34
5. Cellulose (No. 4 mercerised) .	1·662		1025	0·0227	all	0·00	1·0
6. Cellulose (viscose silk) . .	4·753		1560	0·2466	0·1862	0·76	2·4
7. Oxycellulose (from No. 5 by ozone)	2·00		660	0·0550	0·0193	1·11	0·66
8. Lignocellulose (jute)	1·869 {	(a)	210	0·3291	0·0010	9·4	—
		(b)	950	0·0357	0·0127	—	0·90
9. Lignocellulose (beech wood)	2·600 {	(a)	400	0·6909	—	12·68	—
		(b)	660	0·0148	—	—	0·50

* (a) represents portion of distillate reacting to aniline acetate ; (b) is the portion subsequently obtained active to the aniline alcohol reagent.

These results show that the condensation which produces furfuraldehyde takes place rapidly and is almost completed, before the hydroxymethyl derivative begins to distil over. The aniline acetate test therefore differentiates the aldehydes and no error in the estimation of pentosan is made if this indicator is used. It is noteworthy also that jute and beech-wood, which contain a high proportion of pentosan, yield very little of the hydroxyaldehyde. Its constant presence, however, in distillates from cellulose, starch, etc., render previous determinations of ' methylpentosan ' open to considerable suspicion. Fromberz (*Zeit. physiol. Chem.*, 1906, **50**, 217, 241), for example, obtained the following results with the Kröber-Ellet-Tollens method :—

	Furfuraldehyde per cent.	Methyl-furfuraldehyde per cent.
Wood (extracted with alcohol-ether)	12·68	0·43
,, (6 times treated + NaOH) .	2·29	0·50
,, (9 times ,, ,, } .	2·27	0·50

It will be observed that while the pentose constituent represented by the furfuraldehyde obtained is rapidly dissolved by treatment with sodium hydroxide, the methylpentosan remains unchanged in amount. This in itself is improbable, but it will further be noticed that the amount of 'methyl-furfuraldehyde' obtained agrees closely with the amount obtained by the authors from beech-wood and shown to consist in all probability of ω-hydroxymethyl-furfuraldehyde derived from the cellulose of the wood.

*   *   *   *   *   *   *

A great deal of attention has been given in the last few years to the chemistry of 'lignin.' This complex, which is isolated by the Cross and Bevan chlorination treatment in the form of 'lignone chloride,' $C_{19}H_{18}Cl_4O_9$ (in the case of jute), can now be obtained very simply by the use of 42 per cent. hydrochloric acid, following the observations of Willstätter on the action of this acid on the cellulose portion of lignocelluloses.

To what extent the product thus prepared resembles the original lignin constituent of the wood-complex is uncertain, but it must depend on the relation of lignin to the complex as a whole. We do not recall any recent researches dealing with this problem. The theory of Wislicenius (1910) that the lignin and the carbohydrates of the lignocellulose are united on the basis of the force of surface tension is a very valuable one, in agreement with the structural and chemical conception necessarily to be assumed for such complexes. A union of this order is more probable than a purely chemical one, though the intermediate view that union takes place between carbohydrate and lignin in virtue of the supplementary valencies of the oxygen atoms of hydroxyl groups deserves consideration. Some isolated observations tend to support the hypothesis of Wislicenius. Thus W. Robinson (p. 19) has observed that wood, when subjected to strain, shows, in the area of failure, colour reactions (with iodine and sulphuric acid, chlor-zinc iodide and other re-

agents) characteristic of cellulose, although the lignone reactions with phloroglucinol are still given in the area (Plate II., *a*).

Similarly, we note that in cutting wood sections with a razor the last section often shows the blue colour with iodine characteristic of cellulose, and in the case of flax and hemp, sections taken along the cross-markings react as cellulose, differing from the rest of the fibre. Robinson suggests that in some way the cellulose present in the lignified walls has been unmasked by mechanical strain. The general behaviour of the cell-walls is connected with the micellar hypothesis of cell-wall structure (Nägeli). The microscopic appearances accompanying the deformation of wood by tensile and compressive stresses differ in the much smaller slipping which precedes rupture in tension than in compression and in the differences in the inclination of the planes of slipping. These can be correlated with the differences in the values observed for the strength under these stresses. The author explains this mechanical anisotropy, as well as the double refraction and visible structure of the cell-walls as due to mechanical causes operating on the substance of the cell-wall in the course of its development from a highly viscous fluid to a more rigid condition.

The paper on 'Lignone Reactions,' given below in full, treats of the lignocellulose complex as a whole, particularly in relation to the action of hydrolysing acids and the reactivity of lignocelluloses with phloroglucinol, while the researches of Klason, Häggelund, and others to follow, deal more especially with the chemical properties and constitution of isolated 'lignin.'

LIGNONE REACTIONS AND CONSTITUTION.

C. F. Cross and E. J. Bevan (J. Soc. Dyers and Col., 1916, **32**, 135).

The colour reactions of the lignocelluloses are not primary characteristics of the lignone complex : they are secondary

reactions, that is of derivative and associated groups, which can be modified by various treatments in such a way that their specific reactivity disappears. These treatments are of no marked intensity, the accompanying weight changes are negligible, and the main reactions of the lignone are unaffected. The simplest treatment is that of reaction, obviously of synthesis, with hydroxylamine. The reaction with this base is rapid and the proportion required to suppress colour reaction with arylamines and phenols is fractional.

The following are particulars of a typical experiment. The jute lignocellulose was purified by boiling in 0·50 per cent. solution NaOH, washed and treated with 0·5 per cent. of its weight of NH_2OH in the form of a solution of the acetate, dried down and heated for some time at 100°, thoroughly washed, and again dried. The product was found to contain 0·18 per cent. nitrogen, obviously in the form of the NOH residue (aldoxime). It has been previously shown that the reactive constituent group is an aldehyde, and a furfural derivative, either a hydroxyfurfural or a methylhydroxy-furfural. On the assumption of a molecular weight 111 to 126 the aldoxime would represent approximately 10 per cent. N, consequently for the percentage fixed we may estimate a maximum proportion of 1·8 per cent. of reacting aldehyde groups. It is found, however, that much less is required to reach the point of disappearance of the characteristic colour reactions. It is probable therefore that a proportion of these groups exist in combination, e.g. in acetal union with the OH groups of the β-cellulose.

Although from these facts it is clear that the colour reactions in question are rather adventitious than essentially characteristic, it is not less true that they are so uniform as to afford a quantitative measure of lignone in the lignocelluloses in their natural state of equilibrium—and in effect two of the reactions have been adopted as the basis of quantitative methods of estimation of the latter in admixture with the non-reactive celluloses,

This uniformity of reaction, i.e. of colour intensity of products of direct synthesis, deserves a passing mention in relation to the general question of invariability of the products of cell life.

The lignocelluloses are of the widest possible distribution and extremely diversified as to structure and conditions of aggregation : they also discharge numerous and different functions. It is unnecessary to remind ourselves of the complexity of constitution of the lignocellulose substance, and more particularly of the lignone component. With this many-sided variability and complexity, the group is equally characterised by invariability. But empiricism has inferred a too rigid order of invariability ; and notably has been deceived in regard to the colour reactions now under critical examination.

A revision of the phloroglucinol reaction, long accepted as the basis of one of the well-known quantitative methods, has divided it into two phases or stages, viz. :—

(1) With development of colour, the maximum effect being obtained with less than 1 per cent. of the phenol.

(2) Further combination in much larger proportion, viz. 3 to 6 per cent., and without production of coloured products.

It has been further shown that the weight relationships of phloroglucinol to lignocellulose reacting are constant, and that quantitative methods based on these constants are entirely trustworthy. This matter, of some importance to technologists, is the subject of a recent paper by Max Cline, of the International Paper Co., U.S.A., communicated to the American Paper and Pulp Association under the title 'Ground Wood in Paper, Possibilities of Accurate Determination' (*World's Paper Trade Review*, London, Oct. 22nd, 1915). The immediate occasion of this review was a case of critical difficulty in regard to the composition of two samples of paper which were referred to four different laboratories of specialists, for estimation of

the fibre 'furnish.' The percentages of 'mechanical wood' certified were :—

		Sample 1.	Sample 2.
Laboratory A		50	45
,,	B	31	29
,,	C	35	40
,,	D	30	25

These extensive variations are referred to the unreasoning reliance upon the older method of observations of colour intensity, as against the adoption (Labs. B and D) of methods based upon weight constants. The particular cause tending to falsify the colour observations lay in the special features of the fibre mixture or 'furnish' of the paper, viz. an exceptionally low boiled sulphite pulp mixed with an exceptionally resolved 'mechanical' pulp. While the gravimetric constants were equal to the ordeal, it proved particularly fatal to colour-scale tests. The authors' conclusions make it clear to a critical observer that the adoption of these methods, which speciously commend themselves as simple and facile, has been rather in the interest of the stationer's office or laboratory boy, than of the research chemist, and that our present position accords with a definite stage on the road from empiricism to constitutionalism.

It is the constitution of the lignocellulose which is the problem of perennial attractiveness, and is the main theme of the present communication.

In a previous discussion ('Cellulose Researches,' III.) we have summarised the positive knowledge which we possess (1914) of the lignone complex, in a tentative schematic formula, which comprises a diketo R. Hexene group, a substituted hydropyrone group, ketene groups, and an aldehydic side chain, probably uniting the first group with the β-cellulose.

We anticipate the further discussion of this formula by pointing out at this stage that it does not include an actual

furfural (derivative) group; we have, in fact, ignored this particular component of the natural complex, for the reasons above set forth. It is fractional in amount and has a labile variability.

It is to be stated as relevant to this point that the evidence for regarding the colour reactions with amines and phenols as limited to aldehydic groups is that the major reaction with phloroglucinol is not affected by previously acetylating the lignocellulose by treatment with boiling acetic anhydride, under which conditions all aldehydic groups would be either converted into orthoacetates, or combined by interior reaction within the complex.

Another point to be noted is that under the action of strong aqueous hydracids, e.g. 33 per cent. HClAq at $15°$, the conversion into the 'dehydro-lignocellulose,' with attendant profound structural changes, is marked by complete loss of colour reactivity, and by almost complete elimination of furfural-yielding components (furfuroids). The reaction of this residue with phloroglucinol takes place in identical proportions as with the original lignocellulose. These observations indicate that it is the more resistant R. Hexene groups which condense with the phloroglucinol in the main reaction.

Our attention may now be diverted from this discussion of theoretical points, conveniently to a demonstration of these colour effects and a consideration of some matters of experimental detail.

In the range of colour effects the action of hydroxylamine may be demonstrated as an effect of resist or discharge in relation to those of arylamines and salts. The rapidity of the aldoxime reaction is noteworthy.

In regard to phloroglucinol, the resistance of the aldoxime is also complete; but the presence of the auxiliary hydracid (HCl) induces a gradual breakdown of the oxime, and colour reaction supervenes.

The experimental results following are in development of previous publications, viz. :—

Cross, Bevan and Briggs (*Ber.*, 1907, **40,** 3119), ' Researches on Cellulose,' III.

Comparison of Lignocelluloses.—In the empirical method devised for quantitative work, we have been careful to maintain constant factors of reaction, and the comparison of our results with those of other laboratories shows close agreement of figures for percentage weight of phenol combining. For the purpose of the process of estimation we have expressed the results in terms of the actual phenol substance weighed, i.e. $C_6H_6O_3 . 2H_2O$. On this basis we have figures for a number of specimens of jute, raw fibre, 'scoured,' and bleached, and they lie within the limits, for phloroglucinol absorbed, 3·1 to 4·2 per cent., dry fibre.

Similarly for woods, wood meals, ground wood, our numbers lie within the limits, phloroglucinol absorbed 6·8 to 7·8. It is thus shown that the reaction is proportional to the percentage of lignone, of which again the particular reacting groups are a constant proportion, and although the lignone components of woods and other lignocelluloses certainly present constitutional variations which are quite marked, these groups and their reactions are to be taken as constants.

The time factor for reaction under the conditions standardised for the quantitative method has been investigated with the following results : (*a*) A jute weft yarn, purified by alkali scour, souring, washing, and drying. (*b*) Ground wood in form of a fine meal, conditions as in standard process : 2 grams fibrous material with 40 c.c. of 0·5 per cent. phloroglucinol in 10 per cent. HClAq.

Time—10 mins.	1 hr.	4 hrs.	8 hrs.	16 hrs.	
Ligno- $\{(a)$ 0·77	1·10	2·18	2·32	3·1	$\}$ Phloroglucinol
cellulose $\{(b)$ —	5·20	5·95	—	6·84	$\}$ combining

The reaction is much more rapid in the case of the denser perennial lignocellulose. The duration which was selected for

maximum reaction in the case of the standard process, viz. sixteen hours, is therefore confirmed.

Maximum Reaction.—To arrive at a maximum figure for lignone-phloroglucinol combination, it would appear necessary to increase the concentration of the phenol, which, however, implies lowering the concentration of the acid medium. We have adopted a compromise based upon some special observations we have made of the concentration equilibrium of volatile acids, when spontaneously evaporated in contact with pure cotton cellulose.

Aqueous acids of 5 to 9 per cent., say N/5 strength, concentrate to 20 to 30 per cent. by air drying in contact with the fibre : hence the following conditions for the maximum effect in presence of HCl :—

Wood meal 5 grams, phloroglucinol 0·5 gram, dissolved in 15 c.c. water ; added 1 gram HCl (in the form of 3 grams 33 per cent. HClAq), ground together and moist mixture, air dried in porcelain dish ; after four days to 13·6 grams, final air-dry weight 7·5 grams.

This air-dry product contained 0·511 HCl, which, calculated on 2·5 grams increased weight (water) plus 0·4 moisture of original air-dry, represents an acid of 17·6 per cent. (HCl) concentration. The residual phloroglucinol was estimated, and the maximum figure resulted—8·9 per cent. $C_6H_6O_3$. $2H_2O$ calculated to dry lignocellulose, or 6 per cent. (anhydrous) $C_6H_6O_3$ per 100 lignocellulose.

The investigation was then extended to pyrogallol under identical conditions of mixture and digestion.

After air-drying the mixture with the phenol HCl solution similarly to an acid concentration of 17·8 per cent. HCl (estimated), the residual pyrogallol was estimated, and it was found that reaction had taken place in the ratio : 7·6 pyrogallol ; 100 lignocellulose.

The particular point of the reaction with the pyrogallol is

that it disposes of the suggestion of combination of either phenol by 'adsorption.' It may also be mentioned that the lignone-phenol compounds in question are extremely stable and resist all simple hydrolytic actions. Moreover, they do not react with ferrous or ferric salts as do the original phenols.

Action of the Hydracid.—It is clear that the HClAq (10 to 20 per cent. HCl) in these reactions plays an active rôle. There is a disintegration of the fibrous lignocellulose, and the jute fibre will undergo in sixteen hours' digestion losses of weight of 2 to 3 per cent.

The directions of attack are best seen under (i) the action of acids of maximum concentration, and (ii) in contrasting with the action of HClAq that of the saturated solution of the hydracid in ether. Important constitutional points are established by the following :—

Jute fibre digested with twice its weight of concentrated HClAq (33 per cent. HCl) for six days at ordinary temperature.

The fibre substance exhibited changes of colour, through red-brown to olive-green. The product, entirely disintegrated, was washed, dried, and weighed. The loss of weight sustained was 17 per cent. It yielded traces only of furfural on boiling with HClAq (12 per cent. HCl), viz. 0·15 per cent., and gave none of the colour reactions characteristic of furfural derivatives.

The furfural from products soluble in the original acid solution amounted to 5·2 per cent. of the lignocellulose. There is, therefore, a 'destruction' of furfuroids represented by 8·0 − 5·35 = 2·65 per cent. of furfural.

Volatile Acid.—To determine this, a portion of the original acid solution was neutralised (NaOH) and evaporated to dryness. The crystalline residue was exhaustively extracted with strong alcohol and the filtrate again taken to dryness. The residue was taken up with water, acidified (H_2SO_4) and distilled from Ag_2SO_4. The volatile acid obtained amounted to 3 per cent. (calculated as acetic acid) of the original lignocellulose.

The disintegrated product was then subjected to oxidation by CrO_3, in presence of excess of $N/1$ H_2SO_4 in the cold.

The volatile acid obtained by distillation of the solution, and calculated to the original lignocellulose, amounted to 6 per cent. calculated as acetic acid. The neutralised distillate was treated with $KMnO_4$ in excess, and again distilled from H_2SO_4 (and $FeSO_4$). The amount finally obtained showed an increase, viz. to 6·95 per cent. It appears, therefore, that in the first distillation some more complex ketonic acid was present and finally oxidised by $KMnO_4$ to acetic acid.

What is noteworthy is the considerable increase of the acetic acid obtained by this particular method of breaking down the lignone complex. Taken together with the loss of furfural, it is a fair interpretation of the reactions that furfural groups, or furfuroids in process of condensation, are ruptured to form levulic acid, or a ketonic acid of similar type.

Alternatively, we have studied the action of ethereal HCl, the fibre substance being digested for eleven days at ordinary temperatures, then washed with alcohol and finally with water.

The disintegrated fibrous product weighed 86·3 per cent. of the original, that is, the latter had sustained a loss of 13·7 per cent. under the treatment.

It is particularly noteworthy that the product showed the ordinary colour reactivity with arylamines and phenols. We know from the researches of H. J. H. Fenton and his fellow-workers (*J. Chem. Soc.*, **73**, 554; **75**, 427; **99**, 1193) that the ethereal hydracids determine condensation to furfural derivatives, especially in the case of ketoses and their complex colloidal derivatives. We have therefrom a certain confirmation of the view that the colour reactions of lignocelluloses are those of derivative and associated furfural products.

We further examined the products as follows: From the ethereal-alcohol-aqueous washings the ether was removed by evaporation, the solution then neutralised (NaOH), taken to

dryness, the residue exhausted with alcohol, filtered and, after removing the alcohol, distilled from $H_2SO_4 + Ag_2SO_4$. No volatile acid was obtained.

This is to be contrasted with the general action of the mineral acids on the lignocellulose, which is to form acetic acid in some quantity (6 to 7 per cent.). Either acetic acid was not formed under the action of the ethereal hydracid, or was present in solution as an ester. There was, however, no evidence of the presence of ethyl acetate, and the observed results are consistent with the general action of the ethereal hydracids, which is to condense to cyclic compounds, rather than to rupture these.

The disintegrated fibrous residue was analysed for elementary composition :—

		(a)	(b)	Mean.
C	. .	48·31	48·23	48·27
H	. .	5·99	6·11	6·05

and on boiling with HClAq (sp. gr. 1·06) gave 3·6 per cent. furfural.

The reaction with chlorine gas was normal, and after removing the chlorinated lignone-product by digestion with 2 per cent. Na_2SO_3, the residue was a cellulose, which weighed 66 per cent. of the original.

The interpretation of these results is that the ethereal hydracid chiefly attacks the cellulose and more particularly the β-cellulose (furfuroid) of the lignocellulose forming condensed upsaturated groups, which may be of the furfural or keto-hexene type.

It might appear that this is inconsistent with the reduction by 50 per cent. of the furfural obtained as such by the ordinary process of boiling with the aqueous hydracid; on the other hand, it is important to remember that furfural is obtained in maximum proportions only from the saturated

C_5 hydroxy-aldehydes, pentoses and pentosans. It is doubtful whether intermediate products of condensation containing

OH . CH—CH . CH$_3$ groups would yield any large proportion of actual volatile furfural or methyl furfural. We may once again call attention to the limitation of furfural and methyl furfural condensation to pentoses and methyl pentoses, which is still largely current in physiological chemistry, in spite of the fact that it obviously obscures important genetic relationships of the carbohydrates and derivatives.

There is a further consideration raised by the above discussion in reference to the schematic general formulæ for the lignone complex, which we have adopted to give definiteness to our investigations. The formula may be stated as under—
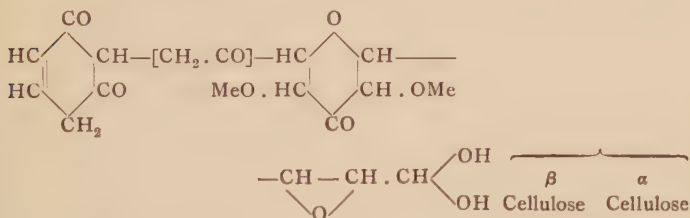
In this formula a number of quantitative results or constants are summarised :—

(1) The quantitative statistics of reactions with chlorine, including the composition of the lignone chloride.

(2) The reactions with bisulphites—the composition of the lignone sulphonates, and their halogen derivatives.

(3) The maximum production of acetic acid by hydrolytic and oxyhydrolytic decomposition.

(4) The statistics of such selective and destructive oxidations as by CrO_3.

(5) We may mention that the study of the oxidations determined by ozone in relation to our schematic formula, has led

M 2

to a recent general confirmation of this constitutional picture of lignocellulose matter (C. Dorée and M. Cunningham, *J. Chem. Soc.*, 1913, **103**, 677).

In relation more especially to (3) and (4), we have to contrast the effect of oxidation by CrO_3 in presence of N/I H_2SO_4 Aq and of $N/5$ H_2SO_4Aq, both in large excess. In 'Researches on Cellulose,' III., pp. 102-3, we give the results of oxidising 100 grams of jute with 42 grams CrO_3 in 2,000 c.c. of N/I H_2SO_4 at ordinary temperatures.

The products of oxidation estimated were—

Acetic acid	.	.	5·2 per cent. of lignocellulose
Oxalic acid	.	.	4·8	,,	,,
Carbonic acid	.	.	4·1	,,	,,

These are relatively large percentages, calculated to the lignone (20 per cent. of lignocellulose), from which they chiefly derive.

In contrast with this, we have oxidised the lignocellulose with CrO_3, increased to 90 per cent. by weight of the fibre in presence of the acid of much reduced concentration, viz. $N/5$ H_2SO_4Aq. After seven days' contact the action was judged to have reached the limit. The CrO_3 reduced was found to be equal to 33 per cent. of the lignocellulose. The products of decomposition estimated in this case were—

Acetic acid	.	.	1·7 per cent. of lignocellulose
Oxalic acid	.	.	6·3	,,	,,

and from the comparison with those recorded above we conclude that the yields of acetic acid are a particular function of the attendant conditions as regards hydrolysis. The oxidation was equally complete in the two cases, as evidenced by the oxalic acid produced, and by the oxidised fibrous residue being equally free from unsaturated groups. We are by these results the more justified in regarding the acetic acid produced in these and other decompositions as derived from ultimate ketene and not acetyl groups ('Researches,' III., p. 102).

In estimating the oxidising effects in terms of CrO_3 (= 100) and the lignone complex, approximately formulated as $C_{19}H_{22}O_9$ (= 394), this ratio at maximum figures (see also 'Cellulose,' p. 143) is $C_{19}H_{22}O_9 : 8$ to 12 CrO_3 or $6 \cdot O_2$ to $9 \cdot O_2$, and this does not account for a break-down to end products, i.e. of C_2, C_1 dimensions. We have called attention in 'Researches,' III., loc. cit., to these ratios, but owing to a misstatement the CrO_3 appears as '$2CrO_3$' in relation to the lignone ($C_{19}H_{22}O_9$), which was intended as the short expression of 'twice the weight of lignone of CrO_3.' This in terms of *molecules* is now correctly stated and connected with results of our earlier researches.

Two points appear from these results : (1) Hydrolysis is an important factor of the resolution ; (2) there is a residue of the lignone which, under hydrolysis and the conditions of reaction, may appear as a component of the fibrous 'oxycellulose' complex, and not undergo oxidation to end products of $C_2 - C_1$ dimensions.

We have some suggestions from recent investigations as to this more elusive constituent of lignone. We have previously given *a priori* grounds for identifying this residue as a group of pyrone type or configuration.

The compound known as 'maltol' is the particular pyrone derivative which we have studied with a view to develop the suggestions above noted.

Maltol is a methyl hydroxy pyrone, and not, as was long held, a benzene derivative. According to the latest views it is 3-hydroxy 2-methyl-γ-pyrone (Peratoner and Tamburello ; Kiliani) :—
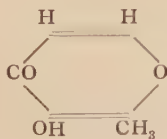
This name arises from its formation in the roasting of malt and suggests that it is a product of resolution of the lignone substance of the enveloping and protecting tissues of the barley.

This is rather confirmed by other points of its natural history. It was originally isolated from larch bark by Stenhouse and Groves (*Proc. Roy. Soc.*, **11**, 405) and described as larixinic acid. It has also been obtained from the needles of other conifers, e.g. *Abies alba* (Feuerstein, *Ber.*, 1901, **34**, 1804).

Maltol has very characteristic properties which we have been able to study by way of an original preparation supplied by C. E. Groves, F.R.S., and also of a specimen of the volatile products of barley roasting, for which we are indebted to W. D. Dick. While confirming the statements of investigators as to its formation properties and reactions, we have taken advantage of the latter in verifying the early formation of maltol in the process of merely heating the lignocelluloses (100° to 200°) as a first stage in their destructive distillation. But rather unexpectedly we obtain the product also from cellulose on heating at 150° in sealed glass tubes. We have also carried out a number of experiments in glass tubes open at one end, heating the cellulose to just visible change of colour. On testing with dilute ferric chloride, the distribution of the reaction product can be followed.

Compare also A. Backe, 'Sur un nouveau Composé conteun dans les Produits Alimentaires' (*Comptes Rendus*, **150**, 541; **151**, 78). This author observes the presence in biscuits of a compound giving the reactions of maltol, but differing in m.p. (95°) and other respects. He assigns to this body the constitution 5-hydroxy-3-methyl-pyrone. Maltol has also been identified in the products of destructive distillation of cellulose (E. Erdmann and C. Schaefer, *Ber.*, 1910, **43**, 2398).

The significance of these observations is probably far-reaching. The directions of proximate resolution of the simpler saturated carbohydrates under conditions of condensation are—

(1) Furfural and derivatives containing CH_3 and OH groups.

(2) Pyrone and derivatives containing CH_3 and OH groups—

$$(1) \quad \begin{array}{c} CH : CH \\ | \qquad \diagdown O \\ CH : C . COH \end{array} \qquad\qquad (2) \quad CO \diagup \begin{array}{c} CH : CH \\ \diagdown \\ CH : CH \end{array} \diagdown O$$
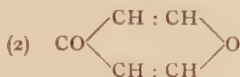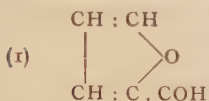
(3) Ketonic acids : saturated acids of the type of levulic acid—

$$CH_3 . CO . CH_2 . CH_2 . COOH$$

and similarly of the celluloses. There is one general characteristic of the mechanism of these otherwise diverse transformations which is the migration of oxygen (OH) and hydrogen in the saturated carbohydrates, and it is further established by the present results that the labile state characteristic of these polyhydroxy compounds is probably at its maximum of sensitiveness in the colloidal aggregates which we know as celluloses and lignocelluloses.

We have already been able to give some definition of this labile state, or sensitiveness (' Researches,' II., Chap. i.), and we note in extension of this, what is now known of the relationships of the various forms of energy to typical celluloses and derivatives.

Heat.—It is well known that the 'hygroscopic moisture' of cellulose represents exothermic combination, therefore in applying heat to cellulose, the first effect is to put it in a definitely endothermic state. This is an important factor of the phenomena of the dye-bath. On continuing to heat there are marked endothermic accumulations which have been diagnosed by various observations (see 'Cellulose,' p. 69) and more carefully described in the 'Thermal Study of the Carbonisation Process,' by Hollings and Cobb (p. 42).

We have now to interpolate beyond this our own observations of the production of the volatile pyrone derivative as the first evident product of the second phase of change under heat.

The relationships of cellulose and lignocellulose to light and to electrical energy have been mentioned elsewhere. We merely mention that the phenomena occasioned are definitely those of the cellulose complex, and we have taken the view that this colloid exhibits a state of matter analogous with that of the solution of an electrolyte. To give these phenomena an extreme expression, we may recount in conclusion some observations which we have had occasion to make, and which lead to the general conclusion that, if to any fibrous cellulose surface any electrolyte in solution is applied, or further, even if the purest form of water is applied, there is some definite change of molecular aggregation set up, and this effect can be brought to visible demonstration by means of reagents which produce colour effects.

*   *   *   *   *   *   *

We (C. and D.) have recently made some further (unpublished) observations on this subject with a view to ascertaining (*a*) effect of the concentration of the acid on the proportion of phloroglucinol combining, and (*b*) effect of the phloroglucinol, which possibly couples with the lignocellulose at several points or groupings, on the resistance of the new complex to various types of resolution.

The jute used was boiled for thirty minutes in 3 per cent. sodium carbonate solution. All results are given in terms of dry weights (water oven temperature).

With regard to (*a*) the following table (I.) is clear :—

I.—*Absorption of Phloroglucinol by Jute in presence of* HCl *of varying concentrations.*

HCl per cent.	1·5	3·0	4·5	6·0	9·0	12·0
$C_6H_6O_3$. 2Aq per cent. combined	0·28	1·23	1·58	2·03	3·19	3·20

Up to 9 per cent. HCl . Aq the percentage of phenol combining is almost in direct proportion to the concentration of the acid employed as medium.

Following up the point raised under (*b*) we estimated the
' lignin ' in jute and beech-wood using 42 per cent. HCl (six-
teen hours in the cold), obtaining normal figures. Very different
results, however, were obtained on applying the same method
to the lignocellulose-phloroglucinol compounds as shown
below :—

	'Lignin' per cent.
Original jute	16·0
Jute-phloroglucinol compound, 3 per cent. combined phenol	75·6
Original beech	30·1
Beech-phloroglucinol compound, 5·1 per cent. combined phenol	76·3

The jute chlorinated for maximum yield of cellulose gave
84·5 per cent. : the 16 per cent. lignin found above is thus
confirmed. The values for the phloroglucinol compounds
show that combination, even with these very small proportions
of the phenol, has determined a new cleavage of the ligno-
cellulose complex under reaction with hydrochloric acid, the
nature of which we are studying at present. We merely record
here some statistics for the 75·6 per cent. residue obtained from
the jute-phloroglucinol compound above. This residue was
dark red in colour and retained the fibrous structure of the
original, although greatly disintegrated. It reacted with chlorine,
the yellow chlorinated lignone developing a crimson colour
with sodium sulphite as usual.

*Constants of the residue obtained from Jute-phloroglucinol compound
by treatment with 42 per cent. HCl.*

	Per cent. on the dry residue.	Per cent. on the original jute.
Loss in boiling 1 per cent. NaOH, one hour	26·4	20·0
Loss in cold 17 per cent. NaOH . . .	20·8	16·7
' Cellulose ' after chlorination . . .	80·2	60·2
Furfural	1·8	1·4
Methoxyl	5·6	4·2

None of the residues from these treatments were normal, in the sense that they were all more or less red or yellow and probably still contained combined phloroglucinol.

The observations are interesting from the point of view of the ' reaction-continuity ' of the lignocelluloses. The lignin complex may or may not be in chemical union with the cellulose complex, yet combination with a proportion of the phenol at some point or points, determines a remarkable resistance of the whole complex to resolution.

RESEARCHES ON LIGNIN. PARTS I. AND II. LIGNIN AND REACTIONS OF LIGNIN. PART III. CONSTITUTION OF PINE-WOOD LIGNIN.

P. KLASON (Ber., 1920, **53**, 706, 1863 ; *ibid.*, 1865).

In an earlier paper (*Ark. Kemi. Min. o. Geol.*, 1917, **6**, 21), the author develops his old theory (1898) that lignin is based on coniferyl alcohol $HO . C_6H_3(OMe) . CH : CH . CH_2OH$. From spent sulphite liquors he has isolated a calcium salt $C_{40}H_{44}O_{18}S_2Ca$ which is regarded as a complex composed of one molecule of coniferyl alcohol $(C_{10}H_{12}O_3)$ + 3 molecules of hydroxyconiferyl alcohol $(C_{30}H_{36}O_{12})$ + $Ca(SO_3H)_2$ − $3H_2O$. A molecular weight of 916 was determined.

Solutions of this salt on treatment with naphthylamine hydrochloride give a yellow compound insoluble in water. After removal of the calcium ligninsulphonate from sulphite liquor, naphthylamine again precipitates a compound of the formula $C_{50}H_{60}O_{14}S_2N_3$, corresponding to a lignin $C_{29}H_{26}O_3$ with 12·3 per cent. OMe. The original calcium salt agrees with a lignin $C_{40}H_{42}O_{12}$ containing 17 per cent. of OMe.

The original lignin might be composed of one molecule of each compound. On destructive distillation of lignin 15 per cent. of phenols are obtained.

The author suggests that lignin is possibly present in wood as a glucoside and that it may be built up from pentose sugars. It is probably a condensed form of methylated cinnamic alcohols and similar substances.

A further examination of the naphthylamine ligninsulphonate (Part I.) leads to the postulation of the acrolein group R . CH : CH . CHO in lignin. Since more of the compound is obtained from old sulphite liquors than from fresh ones it is thought that the above-mentioned grouping is derived from an alcoholic grouping by oxidation and thus that coniferyl alcohol and aldehyde are the principal constituent groups in pine lignin.

The acrolein group appears in sulphite liquors as

$$R . CH_2 . CH . CHO . SO_3H$$

and under suitable conditions is found to give cyclic salts, e.g.

$$R . CH_2 . CH \begin{matrix} SO_2 - O \\ | \\ CH : NH . C_{10}H_7 \end{matrix}$$
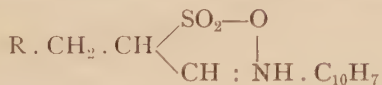
with aromatic amine bases. These cyclic salts are intensely yellow while the normal salts are white. Using this reaction, the author has been able to show that the acrolein group is generally present in woods such as oak, beech, birch, etc.

From the yellow colour of carefully prepared wood liquor the suggestion is made that the flavonol constitutional type applies to lignin, as to many yellow colouring matters.

That part of the lignin precipitated by arylamine bases is designated acrolein-lignin or α-lignin. The other part, which is not precipitated, appears to contain a carboxyl group and is called carboxyl-lignin or β-lignin.

By experimental and statistical observations the formula $C_{22}H_{22}O_7$ is deduced for α-lignin. It is stated to contain one acetyl group which can be eliminated and only one acrolein

group, and putting all the facts together the following hypo-
thetical formula is given :—

$$C_4H_8 \Big\langle \begin{array}{l} C\text{——}O\text{——}C\text{————}C\!=\!=\!=\!=\!=CH\,.\,-CH\,.\,CH:CH\,.\,CHO \\ \ \|\qquad\qquad\ \| \\ C\text{——}CO\text{——}C(OMe)\qquad C(OAc)\!=\!C(OMe)\text{—}CH \end{array}$$
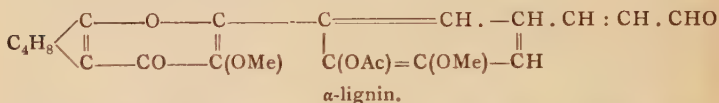
α-lignin.

which contains all the quantitative observations : α-lignin is thus
built on the flavonol type.

By estimations of total lignin and α-lignin in 80-year woods,
the conclusion is reached that pine-wood lignin is composed
of carbohydrate 68, lignin 30, other bodies 2 per cent., and
therefore that lignin contains 63 per cent. α- + 37 per cent.
β-lignin. Making calculations from these proportions and the
known composition of α- and β-lignin, the summation formula
$C_{19}H_{18}O_9$ is deduced for β-lignin.

Since in the sulphite liquors the salt of β-lignin contains
sulphur and calcium in the atomic ratio 1 : 1 it is concluded
that both the SO_3H and COOH groupings are present, and
the simplest assumption is that while α- contains the acrolein
group, β- contains the grouping RCH : CH . COOH.

The formula is supported by analysis which reveals the
presence of one methoxyl group.

That β-lignin contains no free carboxyl group is obvious.
It must be united to the carbohydrate in wood. The simplest
carbohydrates, viz. the pentosans, can, though with difficulty,
be dissolved out of the wood by water (Klason). β-lignin
must therefore be bound to cellulose and probably to α-lignin
also. Lignin cannot well be assumed as a secondary product
derived from cellulose, but appears as a direct assimilation
product of CO_2 and H_2O or formaldehyde. Therefore the
formation of lignin is a function of chlorophyll.

* * * * * * *

These conclusions, viz. that an acraldehyde complex occurs
in lignin and that in the sulphite process a sulphonic acid

$CH_2R . CH(SO_2OH) . CHO$ is first formed, have been the subject of adverse criticism (Hintikka, *Cellulosechem.*, 1921, **2,** 63).

The constitutional type now formulated by Klason for his α-lignin is so specifically divergent from his previous formula based on coniferyl alcohol that the abandonment of the latter should have been explained. This view was critically noticed in 'Researches,' III., and subsequently our own work has led to a general formula of really very similar type to that now proposed by Klason. We suggest also that the ketene linking indicated in our formula (p. 163) is of some importance, and we do not recognise that the production of acetic acid by hydrolysis, direct or indirect, is a necessary proof of an acetyl-ester group.

RESEARCHES ON LIGNIN.

E. HÄGGLUND (Ark. Kemi. Min. och Geol., 1918, **7,** 1-20; Chem. Zeit., 1919, **90** (iii), 186).

Klason regards lignin as produced by condensation of coniferyl alcohol or hydroxyallyl-guiacol (1 mol.) + mono-methylhydroxy allyl-pyrogallol (3 mols.) + hydroxyallyl-pyrogallol (6 mols.), and to contain the two substances $C_{40}H_{40}O_{11}$ and $C_{54}H_{48}O_{18}$. But lignin isolated by the action of $H_2SO_4 . 2 H_2O$ is very far from the original lignin. The present author recommends 43 per cent. HClAq (10 parts) acting on ether-extracted powdered wood (1 part) for fifteen minutes, after which the lignin is filtered off through glass wool. The dissolved cellulose is completely saccharified in a few hours although reversion products (isomaltose?) are present.

The lignin residue from pine-wood amounts to 28 per cent. It contains C = 66·5; H = 5·7; OMe = 14·4; furfural value = 3·7 per cent. Its chlorinated derivative contains

Cl = 41·2 per cent. Some 2·5 per cent. of OMe appears to be split off during the treatment with hydrochloric acid, as most other workers find 16·5 per cent. in this lignin (Klason).

On fusion with potash it gives lignic acids besides protocatechuic and formic acids (but no acetic or oxalic acids). Oxidation yields acetic, but not oxalic acid. On distillation methyl alcohol, acetic acid, and a little acetone were obtained.

The lignin shows the microscopic structure of the woodcells and gives the usual lignin colour reactions, including that with ferric-ferricyanide. It does not, however, show Maule's reaction. It is hardly attacked on heating with bisulphites. Boiled for two hours with 10 per cent. NaOH it loses 15 per cent. in weight, but if treated for three hours at 170° with 5 per cent. NaOH 98 per cent is dissolved.

LIGNIN FROM (WINTER) RYE STRAW.

E. Beckmann, G. Liesche and F. Lehmann (Zeit. angew. Chem., 1921, **34**, 285).

Straw lignin may be obtained under conditions which preclude the possibility of marked change in the product by the action of a 2 per cent. solution of sodium hydroxide in diluted alcohol (alcohol 600 c.c., water 400 c.c.). The mixture is allowed to stand from four hours to two days at room temperature. The reagent dissolves out the lignin, but the pentosans, hexosans, etc., obtained with aqueous alkali are in this case rendered insoluble by the alcohol. The solution is neutralised with hydrochloric acid, the alcohol partly evaporated in a vacuum, and the lignin precipitated by the addition of more acid. Three repetitions gave in total 7 per cent. of lignin on

the dry straw.[1] The lignin is yellow in colour, but darkens and aggregates together at 50° C.

Analyses of preparations made with various modifications of the process gave figures of the following order :—

C = 62 to 63; H = 5·6; OCH_3 = 15 to 15·8 per cent.
Ratio C : OCH_3 10 to 11.

The formula $C_{40}H_{44}O_{15}$ = 765 requires C, 62·8; H, 5·8; OCH_3, 16·2 per cent.; while the formula $C_{42}H_{46}O_{16}$ = 808 requires C, 62·3; H, 5.7; OCH_3, 15·3 per cent.

Molecular weight determinations, by the freezing-point method, gave numbers varying from 768 to 891, so that these values do not agree with Klason's formula $C_{22}H_{22}O_7$ = 405 (p. 172). The lignin reacts readily with benzoyl chloride and its substituted derivatives, either in the presence of alkali or in pyridine solution. Analyses agree fairly constantly with the formula

$$C_{36}H_{28}O_{11} \begin{cases} (OCH_3)_4 \\ (COPh)_4 \end{cases}$$
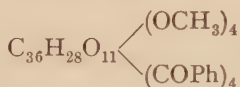
derived from $C_{40}H_{44}O_{15}$ given above.

A table is given from the literature of lignin from which the following extracts are taken :—

Formula.	Atom per cent. calculated.			Method of preparation.	Author.
	C	H	O		
$C_{20}H_{24}O_{11}$	36·4	43·6	20	Synthetic formula from products of resolution of jute.	Cross and Bevan (1913).
$C_{19}H_{22}O_9$	38	44	18	From jutelignin chloride calculated.	Cross and Bevan (1913).
$C_{22}H_{22}O_7$	43·1	43·1	13·8	α-lignin.	Klason (1920).
$C_{19}H_{18}O_9$	41·3	39·1	19·6	β-lignin.	Klason (1920).
$C_{40}H_{44}O_{15}$	40·4	44·4	15·2	Lignin from straw.	Beckmann (1921).

[1] This straw, treated by the fuming hydrochloric acid process, gave, however, a total lignin content of 22 per cent.

RESEARCHES ON LIGNIN.

M. Hönig and W. Fuchs (I. Monatsh., 1918, **39**, 1 ;
II. *ibid.*, 1919, **40**, 341 ; III. *ibid.*, 1920, **41**, 215).

I. Carefully concentrated sulphite-cellulose waste liquor
was made to yield calcium or barium salts of 'lignosulphonic
acid' and these were separated into fractions of different com-
position. The barium salt was thus fractionated into com-
pounds of the following composition :—

$C_{43}H_{50}O_{18}S_2Ba$ with 4 OCH_3 groupings ;
$C_{40}H_{44}O_{18}S_2Ba$ with 1 OCH_3 group, and
$C_{74}H_{114}O_{48}S_2Ba$ with 3 OCH_3 groupings.

The free acids dissolve in water and alcohol and liberate
carbon dioxide from carbonates.

II. These lignosulphonic acid salts were fused with caustic
potash under a variety of conditions, but decomposition was
found to be complete only at 250 to 300° C. Protocatechuic acid
was the sole phenolic product obtained in each case, the yield
being from 13 to 19 per cent. calculated on the 'organic' portion
of the material taken. The opinion is expressed that the
lignosulphonic acids are complicated aromatic derivatives and
that the configuration of protocatechuic acid enters largely
into the building up of their carbon skeleton.

III. The three barium salts when boiled with baryta water
give a number of insoluble compounds and a single soluble
salt $C_{18}H_{30}O_{10}SBa$. The acid isolated from this has the pro-
perties of a tannic acid and appears to resemble those of the
catechu group.

The papers which follow deal with the chlorination process
for the isolation of cellulose from wood and straw :—

THE ACTION OF CHLORINE ON SPRUCE WOOD.

E. HEUSER and R. SIEBERT (Zeit. angew. Chem., 1913, **26,** 801).

The authors take up the work of Cross and Bevan (1895) on the action of chlorine on jute. They recall that in this case a lignone chloride $C_{19}H_{18}Cl_4O_9$ is obtained and that acidity is simultaneously developed. The acid, if calculated as hydrochloric acid, contains chlorine equal in amount to that combining with the lignone.

The authors state that it was never possible to obtain a cellulose free from lignone in one operation when working with wood.

Working at $0°$ C. with steamed spruce wood, four chlorinations of thirty minutes with intermediate extraction with boiling sodium sulphite, were necessary to obtain a lignin-free cellulose. These treatments were continued over a period of twenty-two hours, estimations of (a) the acid formed in each chlorination, and (b) the loss of weight of the wood after each sulphite extraction, being made. Qualitative tests were also made for lignin and oxycellulose. The results, (a) and (b), are expressed in curves (Fig. 9), which show that at the ordinate representing two hours the limiting stage is reached, the lignin has disappeared while the production of oxycellulose has hardly begun. The latter substance then begins to be formed in increasing quantity, the residue after twenty-two hours being a powdery mass of oxycellulose, although the effect of this on the yield of 'cellulose' is very small. So long as any lignin remains it would seem that this is preferentially attacked and oxidised by the chlorine. In this way only can be explained the observation, that at the limiting point (two hours) 31·1 per cent. of chlorine was found to have been converted into hydrochloric acid, while only 9·47 per cent. had combined with the fibre substance. After two hours the production of acidity is

IV.   N

very slow. The fact that it consists entirely of hydrochloric acid is confirmed.

The authors do not regard the colour reactions of lignin with phloroglucinol and aniline as typical, since they disappear after a short exposure to chlorine. Maule's test (permanganate and ammonia) and zinc chloriodide, give more satisfactory results.

The lignone chloride on analysis gave C $= 47\cdot0$; H $= 4\cdot6$; Cl $= 22\cdot6$ per cent. A formula for lignin calculated from these values differs widely from the $C_{40}H_{42}O_{11}$ given by Klason. It is probable therefore that lignone chloride is a mixture. On distillation with hydrochloric acid the substance gave no furfural. On fusion with alkali, oxalic acid was produced in considerable quantity.

THE NATURE OF THE CELLULOSE OF CEREAL STRAW.

E. Heuser and A. Haug (Zeit. angew. Chem., 1918, **31**, 99, 103).

Using the chlorination process for the preparation of cellulose from straw, it was found that the lignin residues are very tenaciously held, and that the repeated chlorination followed by the usual sulphite treatment necessary to obtain a lignin-free product abnormally attacks the cellulose. The authors find that treatment with a 1 per cent. sodium hydroxide solution for ten minutes at 70° C. after each chlorination yields a pure cellulose in a reasonable time (four chlorinations each of half an hour). The yield of cellulose on the dry straw was 54·7 to 55·6 per cent. It contained neither lignin nor oxycellulose, but was not free from pentosans.

In an example given the HCl produced after five chlorinations was 28·5 per cent. and after ten treatments 32·3 per cent.
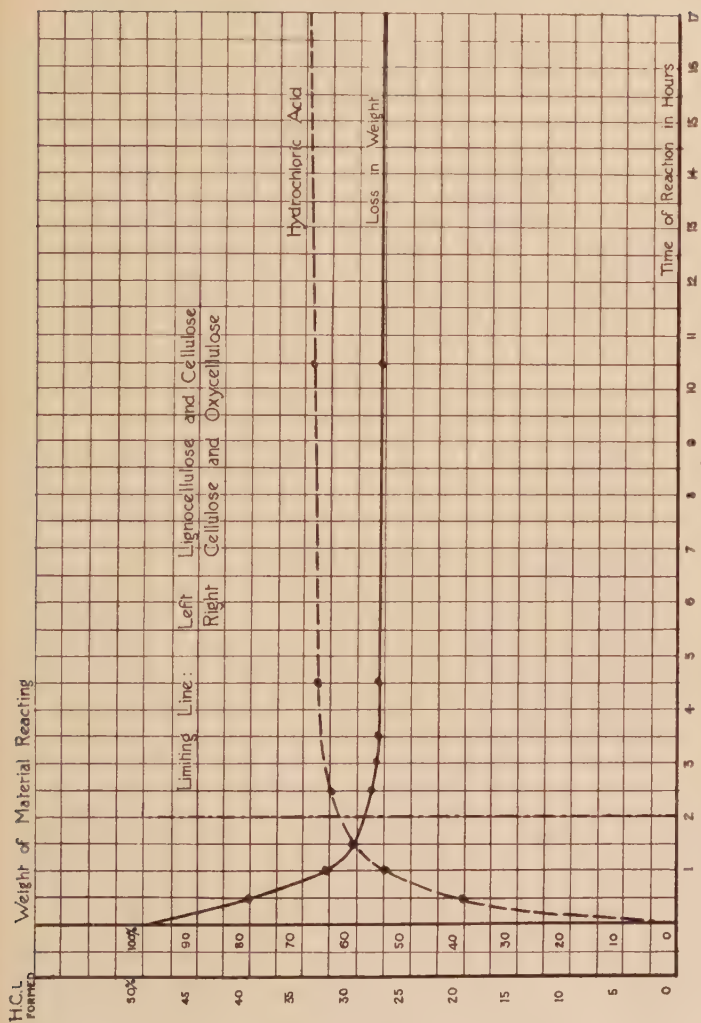
FIG. 9.—Progressive action of chlorine on Spruce Wood (after Heuser and Siebert).

The amount of chlorine combining with the lignin varied from 9·5 to 10·8 per cent.

The nature of the action of chlorine gas on pentosans was examined in the case of an isolated preparation of xylan. The amount of HCl produced was 9·0 per cent. after four hours and 16·9 after fifteen hours, while the chlorine fixed was 16·8 per cent. These values suggest combination by a substitution reaction, but they are not regarded as final. The action is very much slower than with lignin, and only a very small amount of the acid produced during chlorination can be attributed to pentosans.

* * * * * * *

The next section consolidates these various investigations in their application to the analysis of the wood substance on which much attention has been concentrated during the past few years, especially in America. The papers of W. H. Dore, of which we give a full abstract, represent a very complete contribution to the problem and incorporate earlier work. Before dealing with these we mention the following investigation on account of its novel method and the discussion it contains :—

THE DETERMINATION OF CELLULOSE IN WOOD.

B. Johnsen and R. W. Hovey (J. Soc. Chem. Ind., 1918, **37**, 133 T).

In this paper will be found a valuable criticism of the earlier contributions on this subject. The procedure followed by Schorger (*J. Ind. Eng. Chem.*, 1917, **9**, 556, 564) admittedly left a cellulose which still gave a strong methoxy reaction. The authors state that it is not surprising therefore to find that Schorger's values for the cellulose are extremely high and very variable. In the light of Heuser and Siebert's work (p. 177) they cannot agree with Schorger in saying that, to obtain the

cellulose absolutely free from lignin, the error involved by de-
struction of the cellulose is out of all proportion to that caused
by the presence of traces of lignin.

The technique of Siebe and Walter in which all the chlor-
ination and other operations are conducted in a Gooch-crucible
is strongly commended, but though, by this process all the
lignin is removed, the residue on distillation with hydrochloric
acid still gives furfural in quantity. These furfural-yielding
impurities can, it is true, be eliminated by the action of in-
organic acids or by alkaline hydrolysis, both of which, however,
seriously attack the cellulose, making all these methods un-
suitable to exact analysis.

The authors describe their own method of acid hydrolysis
by which, they claim, the cellulose is not attacked, while the
furfuroids and lower carbohydrates are eliminated in large pro-
portion. The reagent employed is a mixture of glacial acetic
acid (60 parts) with glycerine (92 parts) at a temperature of
135 to 140° (for three to four hours).

The values thus obtained for cellulose are 2 to 4 per cent.
lower than those found by the chlorination methods (aspen-
wood 57·4, against 61 per cent). The residues still contain
furfural, methyl-furfural and methyl yielding groups as shown
in the following table, (*a*) indicating the use of the chlorination
method, (*b*) that of the authors :—

Cellulose from		Furfural.	Methyl-furfural.	Total furfural.	Methyl.
Balsam fir	(*a*)	3·87	1·56	5·43	·14
	(*b*)	2·95	1·43	4·38	·14
Aspen .	(*a*)	10·49	1·39	11·88	·135
	(*b*)	8·73	1·43	10·16	·127

In an attempt to diagnose the groupings above mentioned
the wood was treated with various reagents calculated to elimi-
nate one or other of them. The authors conclude, 'the broad-
leaved trees give a considerably higher yield of furfural than

the coniferous woods, which latter contain much more substance yielding methyl-furfural. This substance, or at least a part of it, is very resistant as there always remains a considerable proportion of it in the residue.' The effect of the new acetic acid reagent was most pronounced in effecting its removal. The tables show, however, that 'it was not possible with any reagent to extract only one uniform substance from the wood.' More or less of one substance may be dissolved out, but always in admixture with other non-cellulose constituents. These have given rise to the terms hemicelluloses, hemilignin, protopentosan, etc.

Wislicenus' theory (*Z. Chem. Ind. Kolloide*, 1910, **6,** 1) that the lignin and the carbohydrates of the wood are combined on the basis of the force of surface tension can no doubt be applied to other constituents of the wood, and explains both the uniformity in the composition of the woods and the fact that one constituent cannot be removed without the others.

The Analysis of Woods.

1. **The Proximate Analysis of Woods** (J. Ind. Eng. Chem., 1919, **11,** 556).
2. **Determination of Cellulose in Woods** (*ibid.*, 1920, **12,** 264).
3. **Distribution of certain Chemical Constants of Wood over its Proximate Constituents** (*ibid.*, p. 472).
4. **The Proximate Analysis of Coniferous Woods** (*ibid.*, p. 476).
5. **The Proximate Analysis of Hardwoods** (*ibid.*, p. 984).

W. H. DORE, of the University of California.

The author sets out with the intention of collating methods of analysis which will account for the total constituent elements of the wood. No. 1 contains a full account of certain methods proposed and preliminary trials, e.g. on drying in various ways and its influence on the chlorination figure.

In the second paper the author's conception of 'cellulose,' as applied to material derived from woods, is defined to mean a 'product prepared by processes of sufficient intensity to remove all extractives (resins, dyes, etc.), incrusting substances (lignin), and hemicelluloses (condensed carbohydrates of pentose, mannose and galactose basis), and limited in their action to these bodies. The chlorination process as applied to wood material, treated with non-hydrolysing solvents only, fulfils these requirements.' The residue should be 'free of lignin and hemicellulose. It may contain α-, β- and γ-celluloses (mercerisation test), also furfural yielding complexes, but should be free from easily hydrolysable pentosans.' The following table is held to justify these requirements :—

PRELIMINARY HYDROLYSIS AS APPLIED TO WOODS.

All percentages on air-dry wood (11·6 per cent. moisture).

Method.	Total cellulose.	Furfural from total cellulose.	α-cellulose.	Furfural from α-cellulose.	Ratio of α-cellulose to total cellulose.
1. Chlorination without hydrolysis (Renker).	48·5	2·5	36·6	0·50	0·75
2. Original Cross and Bevan method (1 per cent. boiling NaOH before chlorination) . . .	45·8	2·6	35·4	0·27	0·77
3. Acid hydrolysis (Johnson and Hovey) .	44·25	2·2	34·6	0·26	0·78

In the fourth communication the application of these precepts to coniferous woods is briefly given. The claim is made that by the omission of the preliminary hydrolysis, more reliable results are obtained for cellulose and lignin than by previous methods. The soluble pentosans are determined

in the chlorination liquors; mannose and galactose on the original wood.

The fifth paper, dealing with hardwoods, contains a revised account of the analytical processes worked out by the author, some novel details of technique being given in the third paper. We quote the revised procedure in some detail.

The Proximate Analysis of Hardwoods.

The author's methods for the analysis of coniferous woods, No. 4, have to be modified for hardwoods (e.g. *Quercus agrifolia*) in that (*a*) a digestion with 5 per cent. sodium hydroxide is necessary, and (*b*) that the lignin should be estimated (and this is recommended for all types of wood) by the gaseous hydrochloric acid method (König and Becker, *Zeit. angew Chem.*, 1919, **32,** 155; cf. *J. Soc. Chem. Ind.*, 1919, **38,** 530, A), or by the use of 42 per cent. acid after Willstätter (1913).

The following resumé of the methods is compiled from the contributions mentioned. The sawdust should be fine enough to pass an 80 mesh sieve, but not a 100 mesh. A Gooch crucible is used wherever possible with a filter disc of mercerised cotton.

The procedure is given in order, the same sample being used throughout.

(1) Loss on drying at 100° C. to constant weight.

(2) *Benzene Extract*—Six hours' extraction.

(3) *Alcohol Extract.*—Residue from above six hours with 95 per cent. alcohol.

(4) *Fraction Soluble in Cold Water.*—Residue from (3) digested twenty-four hours, then dried for sixteen hours at 100° C. The percentage weight of the residue is added to the percentage losses found in (1), (2) and (3), the total subtracted from 100, and the result given as 'soluble in water.'

(5) *Fraction Soluble in cold* 5 *per cent. Sodium Hydroxide Solution.*—Residue from (4) is digested with 100 c.c. of the

alkali for twenty-four hours. Dry sixteen hours as before. Loss in weight from the previous weighing gives the result (5).

(6) *Cellulose.*—Part of the residue from (5) treated by method of Sieber and Walter (*J. Ind. Eng. Chem.*, 1920, **12,** 267), i.e. 2 grams on the Gooch crucible, chlorine gas drawn through for twenty, fifteen and ten minutes ; after each treatment with chlorine the mass is treated with saturated sulphurous acid solution, washed, digested with 3 per cent. sodium-sulphite solution for forty-five minutes. Dry sixteen hours at 100° C.

(7) *Lignin.*—The wood after treatments (1) to (5) is placed in a test tube, kept cool in water, moistened with concentrated hydrochloric acid, and gaseous hydrochloric acid passed for two hours. Close up, allow to stand twenty-four hours, dilute, wash and dry sixteen hours.

(8) *Pentosans not otherwise accounted for.*—The filtrate and washings from (6) are concentrated and adjusted so that 125 c.c. (made equivalent to 1 gram of wood) can be distilled with 30 c.c. of concentrated hydrochloric acid and the estimation of furfural continued as usual.

N.B.—The pentosan constituents of oak are partly soluble under (5) ; the insoluble portion chiefly remains with the cellulose.

(9) *Mannose (residual).*—10 grams of wood after treatments (1) to (5) are hydrolysed with 150 c.c. of hydrochloric acid of sp. gr. 1·025 for three and a half hours at boiling temperature. Filter, digest with 100 c.c. of hot water and repeat till 500 c.c. of filtrate are obtained, neutralise with sodium hyroxide and acidify with acetic acid. Concentrate to 150 c.c., add 1·0 gram of phenyl hydrazine in 20 c.c. of acetic acid. Filter after two hours, wash the precipitate with water and finally with acetone. Dry at 100° C. Residue × 0·6 = Mannose.

(10) *Galactose (residual).*—5 grams of wood as above. Treat on a water bath below 87° C. with 60 c.c. of nitric

acid of sp. gr. 1·15 concentrating to about 20 c.c. in volume ; dilute, filter and wash till the filtrate is colourless.   Evaporate at 87° C. to 10 c.c.   In a few days the mucic acid separates mixed with oxalic acid.   Dilute with 20 c.c. of water leaving the mucic acid.   In twenty-four hours filter on a tared asbestos Gooch crucible, wash with 50 c.c. water, 60 c.c. alcohol, and finally ether.   Dry at 100° C.   Residue × 1·2 = Galactan.

(11) *Furfural and Methoxy Distribution.*—For a full discussion on this question see the author's paper (*J. Ind. Eng. Chem.*, 1920, **12,** 473), in which a useful modified method for methoxyl estimation is given, and the question of distribution is discussed.

(12) *Acetic Yielding Groups.*—Three hours heating under reflux with 100 c.c. 2·5 per cent. sulphuric acid.   Filter and wash up to 200 c.c. with CO_2 free water.   Distil under diminished pressure on a bath kept at 85° C.   When nearly all the liquid has distilled, add another 100 c.c. of CO_2-free water and repeat.   Titrate the total distillate.   A correction for formic acid is made.

The sum of these estimations (1) to (10) in the case of oak totals approximately 100·5 ; with the coniferous woods, (5) being omitted, a total of 101·5 is usually reached.

Tables showing the distribution of furfural yielding groups and of methoxyl, in hardwoods, are given.

*   *   *   *   *   *   *

It may be mentioned that Heuser and Wenzel, in an examination of the various methods for the determination of lignin in cellulose (*Papierfabr.*, 1921, **19,** 1177), find that Becker's method (72 per cent. H_2SO_4) gives too high results, as also does the gaseous hydrochloric acid method of König and Rump.   The authors state that satisfactory results are obtained by treating 1 gram of the sample with 70 c.c. of 41 to 42 per cent. hydrochloric acid for eighteen hours, after which the

acid is diluted with ten times its volume of water and boiled for ten minutes. This we can confirm.

A number of authors have described alternative methods for the estimation of furfural, among which we note :—

" Determination of Furfural by means of Fehling's Solution," (1) Eynon and Lane, *Analyst*, 1912, **37**, 41 ; (2) Baker and Hulton, *ibid.*, 1916, **41**, 294.

" Pentosans and Methyl Pentosans in Cereals and Wood Fungi," Ishida and Tollens, *J. Landw.*, 1911, **59**, 59.

" Volumetric Estimation of Phenylhydrazine and its Application to the Estimation of Pentosans," A. R. Ling and D. R. Nanji, *Biochem. J.*, 1921, **15**, 466.

The last-named appears to be sufficiently expeditious to justify a brief account of its technique, which is as follows : The distillate obtained in the usual manner with 12 per cent. HCl is made up to 250 c.c. Of this, 25 c.c. is placed in a 100 c.c. flask, and the acid neutralised with 3N . NaOH, using methyl-orange as indicator and avoiding rise of temperature. Acetic acid is added, followed by 10 c.c. of standard aqueous phenyl-hydrazine solution (about 2 per cent strength), and the liquid is heated at 50 to 55° C. for twenty minutes when the pre-cipitation of hydrazone is complete. The effect of oxygen is reduced during this precipitation by filling up the flask to the neck with water and closing with a cork. After cooling the volume is adjusted to 100 c.c., and, after filtration, the excess of phenylhydrazine is determined in an aliquot portion of the filtrate. Into a flask is measured 10 c.c. of N/10 iodine solu-tion, and to it is added 10 c.c. of the filtrate. The mixture is diluted to 100 c.c. and the excess of iodine titrated with N/20 thiosulphate.

The results agree exactly with those obtained by the phloro-glucinol method.

*   *   *   *   *   *   *

On a general view of the above contributions we note the acceptance of a hydrobenzene-pyrone nucleus as representing

the constitution of lignone, with differences of opinion as to an unsaturated side chain of acrylic type and the actual constitution of the acetic acid yielding groups. In regard to the proximate composition of the wood or lignocellulose complex, and the definition of these in terms of the products of resolution by reaction, it should be observed that these reactions are complicated by the mode of union of the components of an organic complex, originally functioning as a part of a living organism. The separation, estimation and definition of the celluloses of such structures should be subject to this consideration, and so also the whole interpretation of any scheme of proximate quantitative analysis.

CUTOCELLULOSES.

Cutocelluloses.—The protective cuticular tissues which envelop all living structures are complexes of ester-derivatives characterised by fatty ester groups of high molecular weight. Associated with these are waxes, resins and other hydrofuge bodies soluble in neutral organic solvents. Very little attention is given to this group—the cutocelluloses. A systematic research of a particular type is therefore reprinted below.

RAFFIA AND CUTOCELLULOSES—COMPOSITION AND CONSTITUTION.

C. F. Cross and E. J. Bevan (J. Soc. Dyers and Col., 1919, **35,** 70).

The cuticular tissues of plants, with their hydrofuge and other protective functions, have been little investigated by the chemist, and in the modern comprehensive work of Czapek— *Biochemie der Pflanzen*—the section 'Cutinisirte Zellmembranen' occupies three pages only (Vol. I., 577-580), and the bibliography has no mention of any investigations later than 1897.

Cork substance has been more fully investigated, and a number of special fatty bodies of high molecular weight have been obtained as products of resolution, and characterised; but without throwing much light on the fundamental physiological problems, which remain very much as set forth in our work on 'Cellulose' (Longmans, 1895).

The reason for slow progress in this field is the difficulty of obtaining material in quantity; thus, from an apple weighing 40 grams we obtained as finally purified cuticule only 0·08 gram.

On the other hand, the 'raffia fibre,' which is a cuticular tissue introduced to horticulture in this country in 1872, replacing the old-world lime tree bast, or 'bass fibre,' is a massive industrial product, available in quantity, and therefore a more attractive starting-point for investigation.

In view of its important present-day position, the following note from the records of the Royal Gardens, Kew, is of interest:—

'EARLY USE OF RAFFIA AT KEW.

'The earliest record of the purchase of Raffia for use in the Royal Botanic Gardens, Kew, is April 26th, 1872. On that date a bill was entered from Mr. J. T. Anderson for £1 10s. for Raphia. In subsequent bills for deliveries in the period 1872-4 the spelling is changed to Raffia.

'These dates coincide fairly closely with the earlier references to raffia which appear in the gardening periodicals, the earliest reference found being in 1873. In 1874 a note appeared in *The Garden* comparing the qualifications of raffia and bass for certain kinds of work.

'As late as 1883 a good deal of bass (the inner bark of *Tilia sp.*) was used in many gardens for general purposes, raffia being reserved for the most important work. The bass used in gardens was not as a rule received in hanks, but damaged or inferior Archangel mats were cut up for tying

material. When new mats were purchased the ends were very rough, and in order to lengthen their life the ends were properly straightened off and neatly tied. By this means a good deal of tying material as waste was procured.'

Raffia is a complex tissue composed of a true epidermis or cuticle proper, and an underlying sclerenchyma, the cells of which are sufficiently elongated to rank as 'fibres' (illustrated by photo-micrograph of section in 'Cellulose'). On general grounds it might be expected that a constitutional chemical differentiation of the two tissues would cause structural cleavage under the action of reagents. The contrary experience of joint resistance under extreme treatments, while adding to the difficulties of our investigation, has an important significance in relation to the functions of the tissue, chemical and structural.

In regard to the more limited technical aspect and the qualifications for its particular uses, our observations show that it may be regarded as a homogeneous fibrous material.

From the following record of experimental results it will be seen that we have applied the full range of diagnostic reactions which have been adopted in the field of cellulose research; the results are a general characterisation of the tissue, as a chemical aggregate, and a forecast of lines of investigation to to be prosecuted towards a most important scientific and technical goal.

Moisture in air-dry state, average range, 8·0 to 9·0 per cent.

Mineral Matter (ash).—Total (average), 2·7 per cent. Specimen analysed, total 2·21 per cent., containing :—

SiO_3 .	.	.	.	.	.	0·28 per cent.	
Al_2O_3	.	.	.	.	.	0·46 ,,	(trace Mn_2O_3)
CaO .	.	.	.	.	.	0·01 ,,	
MgO	.	.	.	.	.	0·04 ,,	

The ash is fusible and bright green from trace of Mn_2O_3 (oxidised). Two-thirds are alkali salts.

Alkaline Hydrolysis.—(*a*) Treatment with 1 per cent.
NaOHAq—

Loss on boiling 5 minutes . . . . 16·8 per cent.
„ „ 60 „ . . . . 24·3 „

Afterwards exposed to chlorine gas, chlorination of unsaturated
lignone groups took place with formation of 3·92 per cent. HCl.
On exhausting the reaction product with 2 per cent. Na_2SO_3Aq,
the residue was found to be far removed from cellulose and
amounted to 60 per cent.

This resistance characteristic of a cutocellulose complex is
overcome by the more severe action of alcoholic NaOH.

(*b*) Alcoholic NaOH, at 2 per cent. NaOH :—

Loss of weight . . . . . · 39·94 per cent.
Chlorination of washed residue—
  Cl as HCl formed (per cent. of residue) . 7·30 „
  Cl in combination (per cent. of residue) . 4·26 „
Cellulose yield . . . . . · 42·5 „

(*c*) Alcoholic NaOH at 5 per cent. NaOH :—

Loss of weight . . . . . · 46·7 per cent.
Chlorination of washed residue—
  Cl as HCl formed (per cent. of residue) . 6·7 „
Cellulose yield . . . . . · 42·0 „

Combustions of the hydrolysed residue or intermediate product
(*a*), and the 'cellulose' or end product (*b*), established their
relationship in more definite form.

	(*a*)	(*b*)
C	46·41 per cent.	41·74 per cent.
H	6·09 „	6·01 „

With the statistics of chlorination of (*a*) and the weight ratio
a, *b*, it is clear that the groups attacked and removed are a
lignone complex and the numbers conform with a chlorlignone
$C_{19}H_{18}Cl_4O_9$, or an original lignone complex $C_{19}H_{22}O_9$ as
established for the lignone of jute.   It is to be noted, however,

that the ratio HCl formed to Cl combining, which is approximately 2 : 1, shows that the chlorination is accompanied by oxidising effects.

The cellulose reveals the sclerenchyma as ultimate fibres of 2 mm. length. It retains 'furfuroids' represented by a yield of 5·2 per cent. furfural; the original raffia yields 8 per cent. It is evident that the furfuroids are an intimate constituent group, and resistant to severe alkaline treatment.

Soluble Products of Alkaline Hydrolysis.—The characteristic product is a fat acid, ether-soluble, and therefore easily separated; it is accompanied by a 'resinous' acid, the Na salts of which are insoluble in alcohol.

The following data have been obtained :—

Fat acid—yield 11·0 to 12·0 per cent. of raffia.
Composition calc. for $(C_{17}H_{32}O_3)$ C = 70·40 to 70·2 per cent.
,,   ,,   ,,   H = 11·36 to 11·2 ,,
Acid number, Na_2O (for 1 COOH)   10·24 to 10·9 ,,
Acetyl derivative, Na_2O (for 1 OH)   20·1 to 19·0 ,,
Iodine number (Wijs) I.   .   .   .   13·6 ,,
Resin acid yield   .   .   .   .   .   6 to 7·0 ,,
         C = 58·4; H = 10·0 per cent.

Since these bodies are an important chemical characteristic of 'cuticularisation,' the following additional observations may be noted.

On the question of free or uncombined constituents of this group. The raffia contains 3·0 to 3·5 per cent. benzene-soluble bodies.

When broken down by digestion with $ZnCl_2Aq$ (50 per cent. $ZnCl_2$)—by which treatment 25 per cent. of the tissue components are hydrolysed to soluble derivatives—the benzene-soluble bodies are increased to 5·4 per cent. of original raffia.

Acetone extraction of original raffia yields 4 to 5 per cent. of extract.

After the treatment the tissue may be regarded as a 'pure' complex of fibro-cellulose colloids, and shows the following

relation of elementary components (on dry, ash-free substance) :
C 51·8 ; H 6·6 per cent.

When decomposed by a more severe action of aqueous sodium hydrate, viz. taking two parts NaOH by weight, and finishing at 250 to 300°, the resolution takes a different course.

The water-insoluble products, after acidification, yielded—

					Per cent. of raffia.
Soluble in benzene	.	.	.	11·33 per cent. (Na_2O equivalent 7·45 per cent.)
Soluble in alcohol after benzene			7·40 per cent.
Final residue	.	.	.	13·00 ,,
From water-soluble, volatile acid (as acetic acid)	.	.	.	24·9 ,,

The production of volatile acid is to be contrasted with the 5 to 6 per cent. obtained in the simpler cleavage of the complex under the action of alcoholic NaOH, it is also obviously directly related to the destructive resolution of the 'cellulose.'

Owing to present exigencies of space we cannot discuss the contrast of the two modes of alkali attack ; the 'fusion' method is in one direction more profound, especially in resolving the 'cellulose' which, as already noted, is far removed from the normal type. It would appear on the other hand that the oil-resin-acid complex is rather broken away from the cellulose by the resolution of the latter, and appears as a new complex in a less advanced state of resolution as evidenced by the lower proportion of free COOH groups.

There remain to be noticed further variations of the alkali attack, and complementary reactions.

Mercerising Soda (17 per cent. NaOH).—After forty-eight hours' digestion the products were resolved into—

Insoluble	.	.	.	.	.	.	73 per cent.
Soluble	.	.	.	:	.	.	27 ,,

The soluble products were oxidised with hydrogen peroxide in alkaline solution, and on acidification and distillation yielded

38·2 per cent. (of the 27 per cent.) of volatile acids. On treatment with Ag_2O and evaporation, the distillate yielded crystalline $Ag(C_2H_3O_2)$. It was observed that much formic acid was present.

Viscose Reaction.—This resolves the complex into (*a*) water-insoluble (colloidal hydrate) 45 to 50 per cent.; of the water-soluble (*b*), 60 per cent. (30 per cent. of original) was reprecipitated on acidification. Both groups of products contained alcohol-soluble bodies, together amounting to 7 per cent. of the original raffia. From examination of these extracts it was clear that the typical cellulose-ester combination is unresolved.

Benzoyl Chloride Reaction, following mercerisation, and in presence of 7 per cent. NaOH, yielded—

		Per cent. original raffia.		
From soluble bodies	.	9·3 per cent. benzoate.		
From fibre complex	.	111·9	,,	,,
		121·2	,,	,,

This must be taken with the acid-ester reactions (*infra*) in proof of the low proportion of reactive OH groups of the complex. Some further light is thrown on this point by the results of the simplest treatment with alkaline hydrate.

By digestion with $N/2$ NaOH, in the cold for sixteen hours, it was found that the neutralisation of the soda amounted to 3·71 per cent. Na_2O. There was no concentration (adsorption) of the alkali in the fibre substance.

Incidentally to this observation, it was noted that a purple reaction with ferric chloride, characteristic of raffia, was intensified by the alkaline treatment; still more by treatment with alcoholic NaOH. This reaction is similar to that of the tannins, but obviously cannot be ascribed to adventitious components of this group; it is suggestive of a ketonic acid group in the complex, or of a pyrone derivative.

Acid Ester Reactions.—From the foregoing it will be already inferred that the raffia complex is itself of ester character, and

of generally acid function. The typical ester reactions of the cellulose group are only to be expected, in such case, to throw a certain light on the internal equilibrium of the complex.

Nitric Ester.—Treatment with mixture of equal weights H_2SO_4 and HNO_3 (1·5 sp. gr.).

The low yield of nitrate (94 per cent.) is an index of the destructive break-down of the complex. The ester product with 12·71 per cent. nitrogen is an indirect measure of this break-down. The conversion to water-soluble products may be calculated as 45 per cent., and the remainder 'nitrated' in the ratio C_{12} : $(O . NO_2)_5$.

The suggestion is, further, that the complex represented in the nitric ester is in main outline that which survives, as insoluble residue, the attack of alcoholic NaOH : and that the bodies 'saponified' to oil-resin exist in the original complex in some form which implies destructive attack by the nitric acid.

Acetylation.—As a preliminary it was necessary to determine the degree of solvent action of acetic anhydride. The raffia boiled with anhydride for a few seconds lost 4·8 per cent. in weight, but on hydrolysing, and diluting, there was no precipitate and only a faint opalescence.

Prolonged Boiling with Acetic Anhydride.—Yield of product, 105·4 per cent.

The product extracted with benzene gave only 0·13 per cent. extract. On then saponifying, distilling off alcohol, and acidifying, a hydrated colloidal precipitate was formed. The whole was treated with ether. The extraction and dehydration required several days digestion. The ether-soluble was 10·5 per cent. of the original.

It is clear that there is little reaction with the anhydride, or displacement of the oil-resin component of the original complex.

Boiling with Acetic Anhydride and Glacial Acetic Acid.—Yield of insoluble product, 107·7 per cent.

Saponified by N/2 alcoholic NaOH, sixteen hours' digestion in the cold; acetic acid, calculated from NaOH neutralised, 35·6 per cent., residue 73·5 per cent.

By acidifying, and distilling the saponification liquor, the volatile acid recovered was 91 per cent. of that calculated. The difference represents active acid groups derived from the original.

To complete the statistics, the solution poured off from the insoluble, with washings (acetic acid), was treated and yielded :—

Reprecipitated acetylated product   4·72 per cent.
Soluble in diluted liquid   .   .   9·6   ,,
                                         ———
      Or a total yield of .   .   .   122   ,,

The numbers generally approximate to those representing monoacetylation of a hypothetical C_6 unit.

In a repetition of the above, but with the addition of fused sodium acetate, the yield of insoluble acetate was unchanged, viz. 107·0 per cent., the product precipitated from the solution amounted to 6·3 per cent.

The saponification numbers for the main product were higher (acetic acid 42·42 per cent.), confirming an indication in the previous experiment that water is lost in the acetylation reaction beyond the equivalent of the acetyl combining.   This may express an interior condensation or esterification of the original complex.

Acetylation with $ZnCl_2$ as Catalyst.—This leads to a more profound attack and a higher grade of acetylation :—

	Yield per cent. raffia.	Saponification.	
		Acetic acid.	Residue.
Insoluble product . .	57·5 per cent.	59·5 per cent.	51·1 per cent.
Soluble: precipitated on			
hydrolysis and dilution	57·85 ,,	51·63 ,,	61·80 ,,

The numbers represent acetylation to $2\frac{1}{2}$ to 3 acetyl groups on the hypothetical C_6 unit.   The total yield, however, of 116 per cent., as compared with 160 to 180 corresponding with the

above grade of acetylation, is evidence of more profound secondary reactions, and suggests a considerable disruption of the complex.

It remains to note the results of treatments of solution and resolution calculated to accentuate and define special characteristics.

Cuprammonium.—On long digestion the raffia is somewhat attacked, the solution on acidification gives a precipitate of colloidal products, 12 to 14 per cent. of the original.

$H_2SO_4 . 2H_2O$ has a profound action.

The insoluble residue, 23·0 to 28·0 per cent. by weight, is free from furfuroids ; it yields 6 per cent. (of original raffia) only to exhaustive treatment with alcohol.

The solution (diluted) distilled for volatile acid, gave 4·6 per cent. of original raffia, calculated as acetic acid. A portion examined for 'sugars' showed a copper reduction representing (as dextrose) 32·5 per cent. hypothetical cellulose (on original). But a further portion previously boiled to complete the hydrolysis, showed the opposite change ; the CuO reduction was 40 per cent. less.

$H_2SO_4 . 3H_2O$ converts only 40 per cent. of the raffia substance to soluble derivatives.

The insoluble residue contained 2·6 per cent. ether-soluble bodies. After extraction it was saponified by alcoholic NaOH ; the product closely resembled those from original raffia in yields and properties.

Bisulphite digestion at 140° C. for three hours, with a solution made up to 4 per cent. total SO_2 and one-fourth as $NaHSO_3$, reduced 30 per cent. of the raffia to soluble derivatives.

Ether-soluble Products.—

					Per cent. of raffia.
From solution	.	.	.	.	. 0·38 per cent.
Residue	.	.	.	.	. 0·36 ,,

These extracts were resinous.   From this observation and the reduced proportion of total extract, it is evident that the treatment rather consolidates than resolves the characteristic cutocellulose ester complex.   That the lignone groups had undergone the expected resolution was evident in the results of saponifying the residue; the residue being only 41·8 per cent. of the original and approximating to 'cellulose.'

Of the alkali-soluble products of saponification, the oil-resin complex was finally resolved by ether-alcohol fractionation into—

Soluble in ether   .   .   .   .   .   8·4 per cent.
    ,,   alcohol .   .   .   .   .   7·7   ,,

These groups were less sharply differentiated than when obtained from original raffia.   The total yield of 17 per cent. is noteworthy, it is also to be noted that the intimate cohesion of the tissues was unaffected by the bisulphite digestion; from this we may infer that 'cuticularisation' is a structural and chemical process impressed upon the entire external tissue, the lignification of the schlerenchyma is a secondary structural modification.

General Observations.—The water resistant and repellent functions of these cuticular tissues of the plant world are well known to depend in part upon surface secretions of 'free' wax-resin components.   The secretion of these is no doubt a function of chlorophyll which contains an ester group with an alcohol residue of high molecular weight.   Our N-estimations in original raffia give an average figure of 0·75 per cent., which indicates a considerable survival of chlorophyll degradation products.   To this cause of 'hydrofuge' quality there is added that of the chemical constitution of the cutocellulose proper, in such terms as can be given by investigation of products of resolution.   In regard to resistance to oxygen, this is an *a priori* obvious function of these protecting tissues, as well as an inference from the fact that they must be the sphere of oxygen reactions of considerable intensity.

Some measure of this resistance is afforded by treatment with permanganate. The action of the $KMnO_4$ is visibly slight. After sixteen hours' digestion in the cold, the issue is coloured a 'leather brown,' the solution remaining clear. Treatment with SO_2Aq reveals a clearing and bleaching effect. It appears from this that the lignone components of the tissue are constitutionally differentiated from the normal types. This was confirmed by an observation of phloroglucinol absorption which gave negative results. Moreover, there are no colour reactions as with the lignocelluloses of bast fibres and wood structures.

The action of $KMnO_4$ in presence of NaOH is, on the other hand, a destructive oxidation. The following results of an experiment are important :—

Residual 'fibre'	.	.	.	.	.	24·8 per cent.
Oxalic acid	.	.	.	.	.	27·7 ,,
Soluble products—acetic acid			.	.	5·0 ,,

Some effects of nitric acid are specific and will be followed up. A mixture of thirty-six parts glacial acetic acid and two parts HNO_3 to five parts raffia, at 95° C., gave the following results :—

Residue of fibre	.	.	.	.	55·8 per cent.

From this residue, by saponification with alcoholic NaOH, we obtained—

Fat acid	.	.	.	10 per cent. of original fibre.
Residual cellulose	.	.	26·6 ,,	,,	,,

The original liquors from the acid digestion, on evaporating to dryness, gave 48 per cent. residue, of which one-fourth (12·1 per cent.) original raffia was soluble in ether-alcohol, an oil-resin-acid complex. This treatment, therefore, appears to be a non-destructive resolution with maximum yield of the typical components in derivative forms.

Aqueous nitric acid, on the other hand, determines special effects in structural cleavage, especially useful in separating the actual cuticle for microscopic observation. The process can be

followed by naked eye observation to the optimum point, and the product mounted for observation.

An approximate quantitative estimate of the two tissues thus separated, gave—

<div style="margin-left:2em">

Sclerenchyma—Fibre of 2 mm. in length .   .   0·063
Cuticle—Aggregate of serrated cells .   .   .   0·041

</div>

Actual Cuticle.—These observations bring us back to our starting-point, the choice of a mixed cuticular tissue with the necessity of inferential conclusions as to the composition of the actual cuticle.   As we also stated, the true cuticle separated with adhering parenchyma from the apple, potato, etc., may be finally isolated as a residue from the usual hydrolytic treatments, acid and alkaline, which break down the non-cuticular cellular matter.   But, although we obtain the cuticle apparently in its structural integrity, it is a very variable product, the variations being evidently the expression of varying attack by the reagents employed.

The following observations on apple (fruit) cuticle, after isolation and structural 'purification' as described :—

Apple Cuticle (various preparations)—

(*a*) Saponified by 'fusion' process (NaOH)—

<div style="margin-left:2em">

Fat acid separated   .   .   . 46·4 per cent.
Equivalent of acid   .   .   .   9·2   ,, Na_2O

</div>

(*b*) Saponified by alcoholic NaOH (4 per cent. NaOH)—

<div style="margin-left:2em">

Fat acid separated   .   .   . 56·5 per cent.
Equivalent of acid   .   .   .   9·2   ,, Na_2O
Alkali insoluble   residue   from
  saponification .   .   .   .   2·0   ,,

</div>

(*c*) Saponified by alcoholic NaOH (2 per cent. NaOH)—

<div style="margin-left:2em">

Fat acid separated   .   .   . 75·6 per cent.
Alkali insoluble residue   .   . 12·7   ,,

</div>

This residue was actylated, the product remained undissolved in acetylating mixture.

<div style="margin-left:2em">

Yield of acetate .   .   .   . 143·4 per cent.
Ester number   .   .   .   .   50·0   ,,   acetic acid.

</div>

(*d*) Specially prepared, requiring only slight purification with weak alkali (1 per cent. NaOH). This preparation contained 33 per cent. of acetone-soluble components which on saponification neutralised 8·3 per cent. Na₂O. The acid product was 'resinous' with (an approximate) m.p. 210°.

(*e*) This preparation was subjected to elementary analysis—

C, 66·70 per cent.; H, 9·25 per cent.
Acetone extract, 25 per cent.

Elementary composition after extraction—

C, 65·30 per cent.; H, 9·27 per cent.

Saponification by alcoholic NaOH—
Ether-soluble fat acid, 41·4 per cent.

Composition of acid—

C, 68·03 per cent.; H, 10·17 per cent.
Mol. wt. of acid, assuming 1 COOH, 375.
Alkali-insoluble residue, 30 per cent.
Composition, C, 48·4 per cent.; H, 6·06 per cent.

We may briefly, in conclusion, sum up the points established directly and inferentially.

Raffia, though a structural mixture of elements differentiated as to composition, yields an unresolved residue, as insoluble end-product of severe chemical treatments. Of products of resolution three main groups have been characterised: oil-resin-acids, lignone groups, and a 'cellulose' of oxidised type. These, amounting to 75 per cent. of the original, give a sum of elementary components, with similar ratios to those of original raffia; the 25 per cent. not accounted for is probably a complex of similar groups in a less advanced state of elaboration.

The true cuticle of raffia is similar to the cuticle of the apple.

As a cutocellulose, it is extremely resistant to oxidation, notwithstanding the lignification of the sclerenchyma, it does not give colour reactions with phloroglucinol. A purple re-action with ferric chloride appears to characterise constituent

groups of the permanent tissue. The reactions indicate the absence of aldehydic groups.

It is not possible to 'reconstruct' the original complex from a study of products of resolution. With this reservation, its general character is that of an (oxidised) cellulose-lignocellulose ether-ester with acid functions.

CHAPTER VII

CELLULOSE INDUSTRIES AND TECHNOLOGY

As cotton-substance, methodically purified, is the prototype of cellulose, so cotton is the outstanding type of industrial cellulose.

Statistics of the world's production and consumption of the textile fibre reach colossal figures, illustrated by an item calculated to arrest attention even more than the primary data, viz. the progressive *annual increase* of demand, which is estimated at 1,000,000 bales (of 500 lb.).

It is evident from the technical literature of the last ten years, that there is an increasing recognition of cotton as one of the dominant factors of man's world, of its activities and interests which, while immediately those of industry, science and natural history, are ultimately political and international.

These vast and primary aspects of the subject are further illustrated by developments of sectional importance in the direction of further utilisation of 'residual cotton fibes,' the 3 to 12 per cent. of cotton-substance remaining on the 'woolly' seeds after removal of the textile long fibre.

There is a potential supply of 300,000 tons of cellulose from the 5,000,000 tons of the annual cotton seed production of the United States alone; on the world's production of 'woolly' seed, some 10,000,000 tons, a much increased figure.

Towards the realisation of this important economic ideal we owe a great deal to the labour of Ed. C. de Segundo, who

first devised a mechanical treatment of cotton hulls for separation into fibre and shell residue (bran), which produced a supply of 'hull fibre' available for paper-making; and after (1913) invented a machine for de-linting the original seed.

In order of technical progress, measured by increasing concentration of cellulose in the raw material, we note the stages :—

						Cellulose per cent.
'Hull fibre' {	Milled hulls, with separation of bran					50
	E. de Segundo machine	.	.	.		75
Seed lint	„	„	„	.	.	. 85 to 90

The progress in regard to the ultimate form of a bleached cellulose is obviously much greater than in the proportion of the above figures. Not only are all costs of preparation reduced in much larger ratio than that of cellulose concentration of raw material, but 'cellulose quality' is less prejudiced.

The seed lint is now produced in this country by an installation of the de Segundo machines; the systematic work of the inventor has contributed an important chapter of cellulose technology, and a notable advance in realising industrial value from one of the most conspicuous wastes of organic raw material.

The literature of this subject is of great interest to technologists, and students are specially referred to *J. Roy. Soc. Arts*, 1919, **67**, pp. 184-202, 'Residual Fibres from Cotton Seed,' Ed. C. de Segundo.

These short fibre cotton 'wastes' have been largely utilised in the production of nitro-cotton during the war: the supplies are now diverted to the paper mills of America and used in rapidly increasing quantity.

In both industries there are the two major considerations of advantage of this raw material: (1) low cost; (2) uniform standard of quality as unmanufactured material, which facilitates control of essential qualities of the products into which it is manufactured.

We are treating this matter in the inverted order of importance of its subsections, for the obvious reason that cotton-substance, and the non-textile applications of cotton, *as* major subjects, create another perspective.

In accordance with this and our present purpose, we can only mention the investigations of Dr. W. Lawrence Balls, which constitute a chapter of development, not merely personal, but of great importance in linking up 'science' in its 'purest' form with industry.

Beginning with bio-cultural investigations of the cotton plant and crop, Balls has given us an account of his researches in—

'The Cotton Plant in Egypt' (Macmillan, 1912).

'The Development and Properties of Raw Cotton' (A. & C. Black, 1914).

'Analyses of Agricultural Yield' (*Phil. Trans. Roy. Soc.*, 1915-1916).

Continuing his career in organising and directing the Research Department of the Fine Cotton Spinners' Association (Manchester), he is immersed in the complex of problems presented by the mechanical-physical processes of the cotton spinner. An early result of this work and of the systematic study of sampling, grading and valuation of the raw material as a primary factor of the industry, is the invention of his length sorting machine, exhibited and demonstrated at a meeting of the Royal Society of Arts, April 10th, 1918, in illustration of a paper entitled 'Some Instances of Applied Science in the Cotton Trade.'

In this paper the author links up the cotton crop with 'Manchester,' the botanist and agriculturist with the textile engineer, and gives the chemical technologist much material upon which to develop exact knowledge of the borderland phenomena, where chemical reaction is influenced, or determined, by colloid-structural factors.

Balls' researches on the spinning processes and problems are elaborate and comprehensive : it is not for us to anticipate their publication. It will be evident to any technologist that the mechanical properties of a cotton-twist or yarn involve (1) the dimensions and structure of the ultimate fibre including the convolutions arising from the conditions of growth ; (2) its mechanical-physical properties ; (3) the degree of twist ; (4) the true bulk or volume of a structure made up of fibre-substance and included air (air gases) ; (5) the uniformity in terms of weight/length, and apparent bulk or volume, a very important, if secondary, quality in relation to commercial value.

Research work covering this wide field may be expected to have as main results : (1) to confirm, with a more exact definition of rationale, much of the highly developed technique of cotton spinning ; (2) to define the lines of progressive development of the art in terms of exact science.

With this brief notice we direct the attention of students to a subject of first-rate importance, already bearing the impress of the long-continued personal labour of a pioneer worker of distinction.

In the complementary field of chemical technology we notice recent contributions as follows :—

THE EFFECT OF CERTAIN INDUSTRIAL PROCESSES ON THE STRENGTH OF COTTON FIBRES AND YARNS.

R. S. Greenwood (J. Textile Inst., 1919, **10,** 274).

Great divergences of opinion exist as to (*a*) the relation between the strengths of the fibre and the yarn. Thus, 'the strength of a yarn has little to do with the hair strength, only about a quarter of the available tensile strength being realised ; '

and ' yarn does not break primarily through the rupture of the hairs, but through slip of fibre on fibre ' (Balls).

' Single yarns give only 20 per cent. of the breaking strain calculated from the breaking strain of the separate fibres.'

(*b*) The effect of mercerisation—without tension ' a great increase, usually 30 to 50 per cent.,' is noted ; with tension a lesser increase is described. ' There is no doubt that the individual fibres are strengthened, because they shrink in length and increase in diameter 20 to 30 per cent.' (Bowman). On the other hand, ' the increased strength in the yarn represents an increase in the cohesion of the fibres one to another rather than an increase in tensile strength of the fibres (Matthews), and again the increase ' is entirely due to (1) the action of the oil and wax being eliminated, and (2) the greater cohesion of the fibres.'

(*c*) The effect of bleaching—here O'Neill and later, Knecht, claim an increase of strength after bleaching, and according to Matthews, it may be concluded that the tensile strength of cotton yarn is not injured by careful, though thorough, bleaching, and probably may be strengthened by the wetting and pressure causing a more complete binding of the fibres.

To evaluate critically these points, the author has made a thorough investigation. An Egyptian cotton of $1\frac{1}{4}$ to $1\frac{3}{4}$ in. average length was spun into yarn. Tests made at all stages of the preparatory processes, up to and including the spinning process, showed that these had no appreciable effect on the fibre strength.

The following table shows the effect of the various processes alone, and in combination, on the breaking length of twofold yarn (single thread tests) :—

Grey . .	26,136	Mercerised and bleached	30,373
Mercerised .	27,663	Gassed and mercerised	30,053
Bleached .	29,267	,, bleached	30,300
Gassed . .	27,951	Gassed, mercerised and bleached	32,000

Each process therefore has increased the breaking length of the yarn.

Calculations made on the relation between the strengths of yarn and the component fibres show that in the case of the grey cotton the percentage strength utilised is 67, while in the same cotton mercerised and bleached, the percentage becomes 106. It thus appears that a higher percentage strength of the fibres than generally supposed is realised in the yarn.

When mercerised with tension, an increase of 23 per cent· in yarn strength was observed, while the individual fibre strength showed no difference. It is concluded from this that if the fibre is allowed to shrink to the full, no strengthening occurs. A similar result, however, was obtained under tension. This appears to confirm the opinions previously quoted, that the increase in yarn strength is due to a greater cohesion of the fibres, the swelling and untwisting causing the fibres to bind together more firmly.

After bleaching, the yarn showed an increased strength, while the fibre strength was considerably reduced—by 20 per cent. on the average. This again points to an increased cohesion, possibly due to removal of the natural wax.

Results of Tests on Fibres.

Treatment.	Avg. of 100 tests in grams.
Grey	6·77
Scoured yarn (wet)	6·09
„ (dry)	6·94
Mercerised (without tension)	6·87
„ (with „)	6·60
Bleached	5·32
Mercerised and bleached	5·79

*   *   *   *   *   *   *

It will be evident from this paper (*a*) that the problem of measuring physical changes in the cotton-fibre, resulting from

chemical treatments of the fibre-substances, is much compli-
cated by the factors of yarn structure : there is an obvious
further complication in dealing with woven fabrics.

Thus J. Huebner has carried out an elaborate investi-
gation [1] of the '*Effects of scouring and bleaching on the structure
and strength of cotton fabrics*,' which, while supplying important
data to the bleacher, dyer, printer, and finisher for the better
control of his operations, reveals the influence of the secondary
complications of cloth structure, which weakens the claim to
contribute to the elucidation of the primary problems presented
by the fibre-substance.

We are still dealing with cotton as a raw material and basis
of industry, and with problems arising in its more immediate
industrial applications, postponing those which belong rather to
the special chemistry of the fibre-substance (cellulose). We
have to notice briefly, the few industrial developments which
have taken place in other raw materials.

Wood pulps (celluloses) have been used on the large scale
as the basis of nitrocellulose explosives. The celluloses have
been 'purified' by various treatments—generally of restrained
hydrolysis—to a closer approximation to the normal standard
of cotton. One of these (Müller) produces structural modifica-
tions of the fibre which condition an extension of the application
of these pulps in paper-making, in substitution of cotton, giving
effects markedly differentiated from the ordinary characteristics
of wood-cellulose papers.

While this is technically interesting, any industrial value has
to be estimated in terms of costs and in relation to the potential
supplies of short cotton fibres, with the prospective competition
previously discussed.

[1] An account of these researches is since published in *J. Soc. Dyers
and Col.*, 1922, **38**, 29-40 : and should be studied as an example of the
increasingly refined objective of research in this field.

Bamboo as a source of cellulose is of proved value, and paper pulp has been produced industrially on a limited scale.

Papyrus (Cyperus, P.).—

This is one of the most attractive of the potential supplies of paper-makers' raw material. The characteristics of the pulp produced by standard methods have been established as adaptable to the manufacture of the higher grade papers : the papyrus is a 'crop' plant; its growth is massive in all respects, and it promises therefore a production of *prepared* raw material at low cost.

The Walmer Papyrus Co., of Christiania, capitalised to exploit a large concession in Zululand, has, we are informed, exhausted its original capital without reaching the industrial position of continuous production. This apparent failure is probably only a postponement of the contribution of a new raw material, already recognised by paper-makers as of all-round utility and only awaiting the industrial realisation of value.

These arrested developments are in large part to be referred to the world-wide upheaval of the European War, and its especially disastrous consequences to the paper-making industry.

In another direction, and during the war, the industry was called upon to meet the general shortage of raw materials by extempore utilisation of miscellaneous raw materials. In this country attention was directed to the reed growths of our rivers and south coast areas, which were employed in considerable quantity.

The economic working of 'old papers' became an important question, and we notice a valuable text-book of the subject, 'Recovery and Re-manufacture of Waste Papers,' J. Strachan (Aberdeen, 1918), which is also a contribution to the general technique of the art. In this connection we may also notice the authors' critical contributions to the important question of the 'bulk' of papers, and the problem of its exact determination in terms of measured thickness. As a result of this critical

inquiry, we have an instrument of ingenious construction (Strachan's Piezometer).

The applications of paper as the basis of coarse textiles, woven from twisted paper yarns, have been largely developed by the Mid-European countries during the war period. The beginnings of this industry were noted in 'Researches,' I. Under normal competitive industrial conditions, the industry is obviously limited by the inferior tensile qualities of yarns composed of the short fibre units of a paper-makers' pulp prepared by the ordinary beating treatment.

Under the stress of shortage of supplies of the standard textile fibres, the production of these yarns and fabrics reached large dimensions.

This has little permanent significance, that is, as changing the normal industrial perspective, but, on the basis of papers composed wholly or in part of longer fibres, such fabrics would permanently displace a proportion of the textiles made up of yarns produced by the ordinary methods of dry spinning.

The chemical process of hydration of celluloses described on p. 104 (Cross and Bevan, Brit. Pat., 1918) enables the paper-maker to prepare fibres of any length in a condition for working on the paper machine, that is, as a suspension in the carrying water, depositing upon the travelling wire as a uniformly felted mass. By such treatment whole length cotton fibres have been manipulated by the hand-mould process, and finished as uniform 'felts,' or as fabrics of such extreme tenuity as represented by weights of 12 to 20 grams per sq. metre.

It is evident that a technical first principle is thus involved in what appears to be a matter of accident and detail.

A coherent fabric composed of long fibres can be produced as a web in continuous length. Slit into ribbons of narrow width, and treated by the mechanical processes employed in converting paper into yarn, it would yield a 'thread' of novel structure and correlative qualities.

Pursuing this hypothetical development we meet the further questions of advantage in respect of such qualities, and of costs of production. The case is mentioned as an illustration of the wide range of possibilities presented by a critical inquiry into even long-established industrial procedure in the region of the vegetable fibres and their applications.

'*Arghan*' *fibre* is a new raw material claiming attention and study by reason of exceptional characteristics, and also on the ground of potential industrial commercial development. The fibre is a leaf-fibre of a monocotyledon which is stated to be one of the *Bromeliaceae*. The plant, as a fibre-yielding plant, 'discovered' in South America, has been transplanted to the Malay Peninsula for cultivation : and capital has been found for development to the stage of establishing the fundamental elements of technical and industrial value, viz. tensile qualities of the fibre, including resistance to sea water, and high, cultural yields, as a crop product, the leaf yielding 20 per cent. of fibre and the plant having a free growth which ensures easy cultivation and high yields per acre.

The following observations of mechanical-physical properties show the exceptional characteristics of the fibre. As a fibre-bundle, and as an original untwisted unit, it was tested by the method and machine adopted in the silk industry. The 'denier' or weight/length unit, is, m. gram per 900 cm.

Sample.	Denier.	Breaking strain in grams.	Tenacity, gram per denier.	Extension at break, per cent.
1	42	255	6·1	2·0
2	72	259	3·6	1·5
3	39	127	3·3	—
4	100	256	2·6	1·4
5	85	500	5·9	2·5
6	54·6	258	4·72	1·7
7	48·5	298	6·14	2·0
8	58·5	290	4·96	1·9

On the main characteristic of tenacity, these figures translate themselves at sight into *breaking lengths*, the accepted expression

which permits a comparison of all structural materials taking
the form of continuous length. Two of the above specimens
reach the figure of 50,000 m. It has to be stated that the
specimens so far supplied for industrial working, have been
obtained by hand-dressing process : there has been no systematic
selection of leaves, and no systematic study to determine the
optimum of growth condition, nor of treatment incidental to the
separation of the fibre strands.

The composition of the fibre-substance was determined on
an average of the above specimens, with the following results :—

> Cellulose, per cent. . . . . 75·0
> α-Hydrolysis : Loss of weight, per cent. 15·0
> β-Hydrolysis : ,, ,, ,, ,, 21·0
> Lignification—No lignone reactions.

These characteristics are again exceptional, and may reach
a higher level when the fibre is separated by routine process
based on ascertained optimum conditions.

The resistance to sea water is an important characteristic for
fibres of this class, of which the most obvious applications are
in the rope-twine-cord industry. Selected specimens in various
forms were submitted to the severe test of four to six weeks
immersion in an open sea-water tank of a biological station.
The chemical changes of the fibre-substance were relatively
small, and the reduction in tenacity in no case exceeded 50 per
cent.

On the mechanism of the complex attack by the several
possible factors involved, the reader is referred to a subsequent
note of a recent investigation which takes into account all
possible contributories to the disintegrating actions. In the
case of the normal prototypes of fibrous celluloses, and as an
integral effect the attack is so profound as to amount to
complete 'destruction.' This again requires to be studied in
relation to other destructive actions and agencies of the natural

world and order, and especially those of the micro-organisms which effect total resolution of the celluloses to products of low molecular weight. This is the subject matter of a subsequent section (p. 223), and each is a section of the great subject of the 'Natural History of Cellulose' which is in fact the all-inclusive perspective of the matter.

In concluding this section of 'raw materials,' we notice the development of the applications of Kapok fibre in the direction of marine life-saving appliances, which were forced by the war to a position of obviously prominent importance.

The technical basis of these applications is the 'floating' capacity of the fibre in compressed masses, together with the adaptability of a fibre as such, to the confection of appliances in any desired form, best calculated to secure maximum protection to the living body. In both characteristics the fibre is greatly superior to cork and cork substance. The fibre, under strong compression, has an apparent volume of 10 to 12 c.c. per gram. This is obviously due to the high ratio of included air to weight of fibre-substance: this is in part due to the tubular struction of the fibre : in part, to the external structure as a smooth cylinder, and the resilience of the cell walls— which together enable the mass to hold a large proportion of air in the interstitial spaces.

For further information on this matter we refer to *J. Soc. Dyers and Col.*, 1916, **32**, 274 ; *J. Roy. Soc. Arts* (Cantor Lectures), 1920.

Cellulose Industries.—The war period (1914-18) is necessarily marked by developments directly connected with the applications of cellulose and derivatives to war material.

Cellulose Nitrates (Explosives).—The production of these derivatives was obviously increased by expansion, in itself explosive, to colossal dimensions.

It does not appear from the technical records hitherto published that the increase of production was attended by any

changes more fundamental than those of selection, preparation and control of cellulose material in regard to corresponding control of the characteristics of the ester product : the main characteristics being the primary properties of the nitrates as colloids, and the secondary or negative quality of stability.

In the British manufacture the following points of technical-scientific control were established by the researches of Sir R. Robertson and staff : (1) The condition of a purified cellulose is affected and in part determined by the conditions of the treatment adopted as the purifying process. This is specially notable in the case of the alkali treatment, digestion with caustic soda (lye) at elevated temperatures. (2) For maximum stability it is necessary and economical to employ a spinner's long cotton in the advanced stage of mechanical purification represented by sliver.

In a paper by W. H. Gibson on 'The Viscosity of Solutions of Cellulose,' *J. Chem. Soc.*, 1920, **117,** 479, it is first established that the most exact measure of the condition of the cellulose in regard to its physical chemical properties as a colloid, is the viscosity of a solution of standard concentration (2 per cent.) in an exactly standarised cuprammonium : it being also established that the colloidal characteristics of the nitrates prepared from the cellulose under standard conditions are exactly correlative. This communication gives the measured effects of controlled variation of the factors of the process of alkali (NaOH) digestion, viz. time, temperature, concentration of alkali, and proportion to cellulose raw material : also exact prescription for making the standard cuprammonium, and details of precautions essential to be observed in carrying out the preparation of the solutions of specimens of cellulose (effect of light and air), as well as the observations of viscosity.

The Cellulose Cycle of Natural History.

The obvious functions of cellulose in the vegetable world are structural. The industrial uses of cellulose material are

also mainly as structures. In the vegetable world cellulose which has ceased to function usefully is dealt with by various processes which convert it into proximate or ultimate derivative forms which also subserve the constructive agencies of nature. Thus waste crop material, restored to the soil, is converted into humus : in large masses it is converted into peat or lignite and finally into coal. For this aspect of the history of cellulose we refer to a 'Monograph on the Constitution of Coal,' by M. C. Stopes and R. V. Wheeler (Department of Scientific and Industrial Research, London, 1918), in which the subject is excellently reviewed.

Cellulose material deposited in inland waters is subject to a process of destructive fermentation with liberation of marsh gas. These processes have been long known to the naturalist and generally interpreted as part of the cellulose natural cycle. The case of sea water has only recently been followed, although inferred as obvious that cellulose material, deposited on the ocean bed, is also subject to destruction, which, under certain conditions, may be total, i.e. resolution to products of lowest molecular weight.

On this broad theme it will be sufficient for present purposes to notice typical and representative lines of research. The following are specially relevant :—

THE ACTION OF SEA WATER ON COTTON AND OTHER TEXTILE FIBRES.

C. Dorée (Biochem. J., 1920, 14, 709).

Cotton and linen fabrics exposed in large sea-water tanks become completely rotten in three to five weeks.

To ascertain the chemical changes produced in cellulose fibres a purified madder bleach calico was used. Test pieces were exposed, P in the light, Q in the dark. P soon became covered with pink growths which then disappeared to a considerable extent leaving rusty stains. In three weeks P was

falling to pieces while Q, though whole, was quite rotten.   P gave the following results :—

<div style="text-align:right">Per cent.</div>

(a) Loss of weight in boiling 1 per cent. NaOH (5 mins.)   17·44
(b)   „   „   „   (60 „)   17·70
(c)   „   cold 17·5 per cent. NaOH (20 „)   19·15
(d) Hygroscopic moisture   .   .   .   .   .   .   6·09
(e) Copper value .   .   .   .   1·42

The original madder bleach cotton gave under (a) o, under (b) o·6 per cent. loss. Of the part soluble under (c) only 20 per cent. was reprecipitated by acid. It is obvious that a very profound change is produced in the cellulose, as 17 per cent. has become soluble in dilute sodium hydroxide solution.

The variables involved in the action of sea water on cellulose are oxygen, light, and bacteria or mould growth. To study their influence a series of laboratory experiments was set up in which all or none of these conditions were present and each was excluded in turn. The following results were obtained after twenty months' exposure (except sample E which was exposed for twelve months only) :—

Expt.	Oxygen.	Light.	Bacteria.	Relative strength of warp threads.	Change in weight per cent.	Ash, per cent.	Loss of weight per cent. in 1 per cent. NaOH.	Copper value.	
	Exposed to								
Original cotton .	—	—	—	100	—	0·13	5 mins. 0·00	2·4	
A	O	O	O	126	+0·3*	0·21	0·07	2·4	} Least affected —
B	+	+	O	124	−0·4	0·17	0·16	1·7	} bacteria absent.
C	O	+	+	107	−0·6	0·16	0·10	2·3	} Comparatively un-
D	O	+	O	105	+0·8*	0·12	0·52	1·9	} altered—oxygen absent.
E	+	O	+	85	−2·4	0·21	1·80	2·8	} Oxygen and bac-
F	+	+	+	79	−2·0	0·11	0·83	2·4	} teria — most affected.

* Due no doubt to the property of cellulose of fixing mercury from mercuric chloride (Vignon).   This was present in Expts. A and D.

It thus appears that micro-organisms in the presence of oxygen are the active cause of the disintegration. The resemblance of the fibres attacked to the corresponding condition found by Fleming and Thayser in fibres which had undergone deterioration through wet storage was confirmed. The author points out that the changes produced during immersion in sea water are not oxidative or hydrolytic as shown by the constancy of the copper value; they resemble rather the changes produced in cellulose fabrics by the mechanical operation of 'beetling' described by Fort and Cross (p. 17).

Considering the question of rendering cellulose immune to attack in sea water, the author states that it is exceedingly probable that the change, whatever it may be, is conditioned by the reactivity of the three hydroxyl groups of the cellulose unit formula, and it appears not unlikely that if some or all of these were acetylated or otherwise 'protected' the cellulose complex would be unable to rearrange itself in the direction of alkali solubility, and loss of structural character and the deterioration due to beetling or to micro-organisms might not take place. Two cotton fabrics were acetylated approximately to the stage of a mono- and a di-acetate respectively, the structural form of the cotton being retained. These pieces when immersed in sea water showed no growths and after sixteen weeks they appeared completely unaffected. The process can be carried out as follows: one part of fused zinc chloride is dissolved in a mixture of acetic anhydride 5 or 6, glacial acetic acid 4 or 5 parts. The cotton is treated several times with double its weight of this mixture at temperatures below 50°. It is very difficult, however, to acetylate an open fabric such as muslin without largely sealing up the openings and the process is not of much use for marine biological purposes.

Attention was therefore directed to the 'acetate silk' manufactured by British Cellulose and Chemical Manufacturing Ltd., from the soluble cellulose triacetate. An acetate silk twist

yarn was immersed in sea water under the same conditions as those of Expts. P and Q. At the end of five weeks no growths had appeared, the fibres seemed quite unchanged and the breaking load was unaltered. After six months no appreciable change had taken place.

It will be seen therefore that a material is at length available which has a satisfactory resistance to sea water. The yarn is available, and it is recommended that this be knitted into suitable meshed fabrics for marine biological use.

*   *   *   *   *   *   *

The stable normal forms of textile celluloses are thus seen to undergo rapid total disintegration and the agency appears to be primarily the attack of micro-organisms. The conditions of the ocean suggest other contributory physical agencies, but investigation so far shows them as of secondary importance. This aspect is confirmed by the following paper which deals with original cotton, i.e. cotton substance in contact with water and stored under ordinary conditions.

THE DETERIORATION OF COTTON ON WET STORAGE

N. FLEMING and G. THAYSEN (Biochem. J., 1920, **14,** 25 ; 1921, **15,** 407).

It is well known that exposure to damp renders cotton brittle and short fibred and increases its solubility in alkali. As a result, losses of 10 to 15 per cent., due to exceptionally short fibres or 'fly,' are often observed.

The authors first establish the points that moisture in itself has no action, that the damage is caused by micro-organisms always present in raw cotton and that these do not attack cotton unless over 9 per cent. of moisture is present. Thus good Indian raw cotton which contained normally 1·4 millions

of bacteria per gram, showed no increase on this number when kept for three days at 16° C. in the presence of 6, 7, 8 and 9 per cent. of water. With 10, 15, 20 and 50 per cent. of water present, however, the numbers increased to 124, 499, 1112 and 9040 millions respectively under identical conditions.

With a view to tracing the source of this infection, samples of cotton were obtained from India and America, together with a detailed description of the conditions under which each had been grown and harvested. The following results are quoted as an example of many others obtained :—

	Bacteria per gram.	Moulds per gram.	Cellulose decomposing bacteria.	Thermophilic bacteria.
Cotton from open ripe boll not exposed to damp . . .	20,000 *Strepto-thrix Chromogena* only.	50,000 *A. niger*.	+	o
Seed cotton from open ripe boll not exposed to damp .	30,000 *Strepto-thrix Chromogena* only.	100,000 *A. niger ; P. glaucum.*	+	o
Cotton picked and exposed to rain and damp under tarpaulin for two weeks, then ginned.	6,100,000 *Streptothrix Chromogena* with *B. herbicola aur.*	100,000 *A. niger ; R. niger.*	+	+
Cotton exposed five days to damp and rain, then pressed —examined one day later . .	2,300,000 Subtilis type ; *B. herbicola aur.:* B. fluorescens.	200,000 *A. niger.*	+	+

Practically the same flora was present in the American samples, and it is noted that the organisms are all typical representations of soil flora, and that there is no doubt that contamination with soil particles contributes largely to the infection of raw cotton, and other results show that ' at the early stage of the history of raw cottons the wetting to which they may normally be exposed is of far less importance for the

increase in the number of bacteria than is contamination with soil particles.'

In addition to the typical cellulose-decomposing organisms the Streptothrix species were found to attack cotton fibres. The moulds, the coccus, and *B. herbicola aureum* did not attack them.

The authors make use of the swelling test (Balls, 1918, p. 14) to study the nature of the attack of the bacteria on the fibre. 0·1 to 0·3 gram is boiled in 1 per cent. NaOH solution, soured in acetic acid, washed and steeped in 1·5 c.c. of 15 per cent. NaOH solution, followed by addition of 1·5 c.c. of carbon bisulphide. After fifteen to forty-five minutes a test is placed on a glass slide, covered with a slip, and a drop of water allowed to diffuse underneath. Magnified some 50 diameters a normal fibre shows characteristic swelling, the ruptured cuticle forming rings round the fibre, which has the appearance of a series of glass bulbs (Plate IV., *a*).

A fibre that has been attacked by bacteria gives quite different results. Fig. *b*, Plate IV., gives the appearance of a fibre under the action of a streptothrix. The cuticle and most of the cellulose has been perforated in many places and the former has lost its power of resistance, so that the latter swells uniformly—no bulbs being observed. This perforation explains the 'fly' above referred to, which is always attributable to streptothrix attack.

Fig. *c*, Plate IV., illustrates the attack of a cellulose decomposing schizomycete. In this case the destruction of fibre appears to be progressing uniformly from cuticle to interior. The schizomycete causes a general weakening of the fibre, and is only incidentally responsible for 'fly.'

The author has developed the swelling method into a quantitative one for the estimation of the percentage of damaged fibres in a sample. The alkali-bisulphide treated fibres are arranged on three slides and the damaged ones counted. Ten

counts are made on each slide, working up and down and travelling across from right to left. A fibre not attacked along its whole length is not considered deteriorated.

The method is shown to be far superior to that based on alkali solubility, being especially useful in the earlier stages when only a small proportion of damaged fibres is present.

*   *   *   *   *   *   *

It is most important to have established these data in regard to normal celluloses, and it is inferentially obvious that the data apply *a fortori* to the great mass of vegetable organic material. From a limited industrial point of view perhaps more importance attaches to the equilibrium of lignified structures in regard to such destructive agencies whether chemico-physical or bio-chemical. The decay of wood structures although from time to time the subject of careful technical research is a sectional subject which still lags behind in regard to exact knowledge. Some reasons for this are set forth in ' Recent Research in Cellulose Industry,' Cantor Lectures, Royal Society of Arts, 1920 (C. F. Cross), under ' Lignocellulose Types,' the subject of the first lecture.

The extreme resolution of cellulose matter is that of which the products are of C_3 to C_1 dimensions. The active agencies of such are micro-organisms. Our more exact knowledge of these we owe to the researches of MacFadyen (thermophilic bacteria) and Omeliansky (' Researches,' II., p. 151). These observers in their investigation followed the biological method of pure cultures, the action of which is slow, and the laboratory operations requiring long periods for measurable effects. On the other hand, it is a suggestion from natural observation that some of these resolutions are extremely rapid. It is clear that as an industrial process, yielding useful products, such fermentations would require to be of the order of the ordinary alcoholic fermentation. Recent systematic work with this objective has brought about the desired result.

The Power Gas Corporation (Stockton-on-Tees and London) had previously utilised waste cellulose material in various types of suction gas plant, but their technical investigations suggested a more methodical and quantitative utilisation by way of a controlled fermentation yielding specific products.

It is well known that the production of alcohol, or alternatively, acetone, as a source of power in internal combustion engines is a definitely formulated industrial ideal, a subject of clear-sighted discussion, *a priori*, by technologists, and the objective of more than one organised group of investigators.

The various attempts to utilise ' cellulose ' waste material by the most obvious method of conversion into yeast-fermentable forms, have failed to establish an industrial basis ; the method of acid hydrolysis results in a limited conversion (P. Simonsen, *Zeit. angew. Chem.*, 1898), and the costs of treatment are relatively high. Neither in the case of wood-waste nor crop-waste is there any present prospect of an industrial realisation of this ideal of an economic cycle.

After prolonged laboratory trials of their new fermentation process a unit plant has been established and worked by a branch company, registered as Power Spirits, Ltd. Mr. H. Langwell has supplied us with the following notes showing the speed, smoothness and completeness of this fermentation.

The Bacterial Resolution of Celluloses.

Rate of Attack.—The process is of similar character to that of the alcoholic yeast fermentation of sugars or malt dextrins and inverted starch. The solutions require under test conditions, i.e. 5 per cent. inoculation, an incubation period of fifteen hours, but with heavy inoculation, i.e. 50 per cent., an almost immediate start is determined. Once in active fermentation the whole of the cellulose is resolved in twenty-four to twenty-eight hours. The curves (Fig. 10 and 11) show a typical slow charge. They represent the process in terms of gas

evolved from a charge of easy bleaching, sulphite-pulp half-stuff, over the period stated in days.

Varieties of Cellulose Tested.—Our investigations show that any carbohydrate will serve as food for these cellulose-destroying organisms : also that the various carbohydrates yield similar products and in similar proportions under identical conditions.
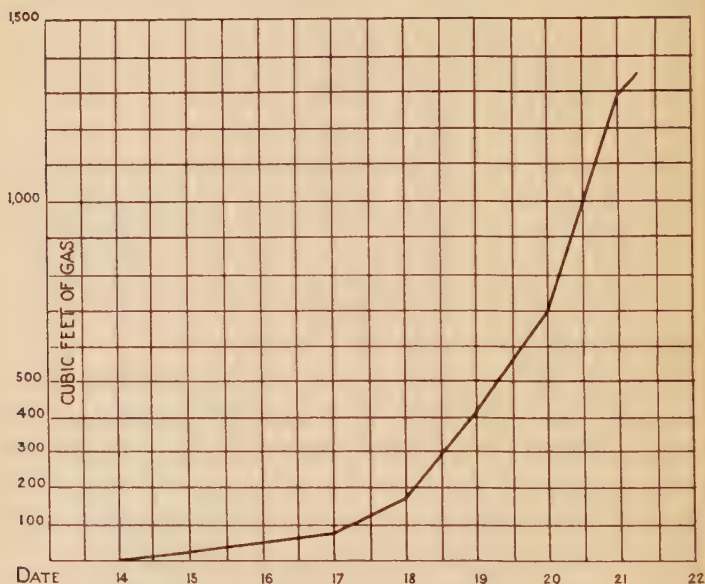
Fig. 10.—Bacterial resolution of cellulose.   (Power Spirits, Ltd.)

The chief difference established is that with increasing complexity (sugar-starch-cellulose) a specifically narrower range of conditions requires to be maintained for rapid fermentation. The following raw materials and transformation products have been tested : reducing sugars from H_2SO_4 hydrolysis (1 per cent. : 100° C. : 2 hours) of megass, bamboo, straws, and wood.   Also dextrose and saccharose.

Starches—rice and potato.

Pure and resistant Celluloses—chemical filter paper, sulphite pulp half-stuff, linen fabric, cotton yarn, viscose silk, mercerised cotton, parchmentised filter paper (H_2SO_4), hydrocellulose (HCl
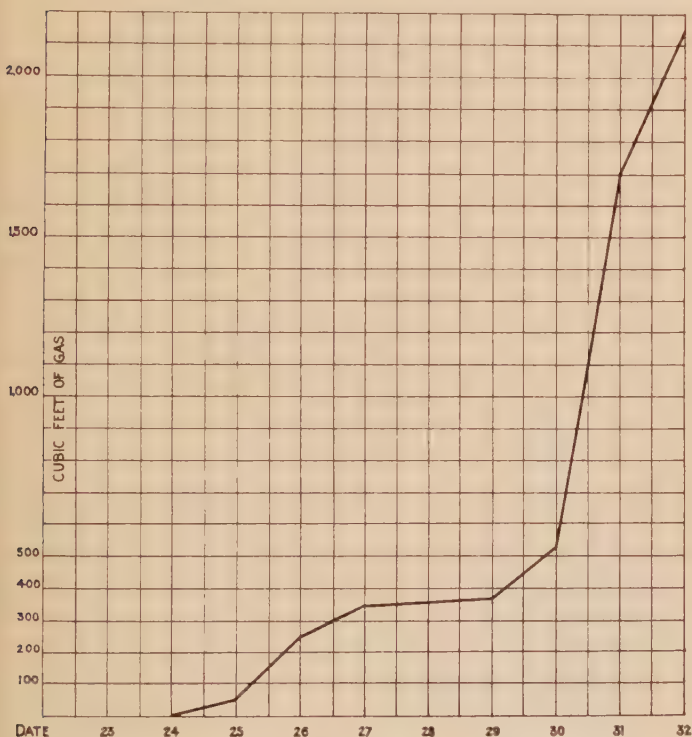
FIG. 11.—Bacterial resolution of cellulose. Typical slow charge.

on filter paper and cotton waste), esparto pulp from soda processes.

Natural hemicelluloses—seaweed, *Lam. digitata*, *F. vesiculosis*, prickly pear, *Op. frins indica*, papyrus pith.

IV.   Q

Natural resistant celluloses from—rice straw, megass, wheat straw, wheat, chaff, papyrus, nettle stems.

Products of Fermentation.—By simple variations of the conditions of fermentation we obtain :—

(*a*) Alcohol and acetic acid : H_2 and CO_2.

(*b*) Acetic acid : CH_4 and CO_2

(*c*) A mixture of (*a*) and (*b*).

(*d*) Reduction products such as H_2S from sulphates and sulphites—FeS and FeO from iron compounds, MnO from MnO_2.

(*e*) Lenco-base of aniline dyestuffs. A yellow pigment characteristic of the bacillus.

From a wide range of quantitative statistics the following hypotheses are deduced, expressed in terms of equations of reaction :—

(1) $C_6H_{10}O_5$ and $H_2O \rightarrow 2CH_3 . CHO + 2H_2O + 2CO_2$.

(2) $2CH_3 . CHO$ and $H_2O \rightarrow CH_3 . CH_2OH + CH_3 . COOH$.

(3) $2CH_3 . CH_2OH \rightarrow CH_3 . COOH + 2CH_4$.

(4) $CH_3 . CHO$ and $H_2 \rightarrow CH_3 . CH_2OH$.

Equation (1) cannot be tested directly as the reagents available to 'fix' the $CH_3 . CHO$ in a synthesised compound are either reduced or interfere with the fermentation. The following have been tried :—

$NH_2OH . HCl$, $NaHSO_3$, $C_6H_5 . NH . NH_2$ and urea.

The results, however, of Neuberg and others render this equation highly probable, and taken in conjunction with equation (2), the following experimental evidence has been obtained:—

(1) The gas liberated is never pure CO_2; there is always either H_2 or CH_4, or a mixture of these two.

(2) Alcohol is never obtained without acetic acid.

(3) A typical gas under certain conditions of working is CO_2 57, H_2 43, and the products in solution are alcohol and acetic acid (ratio 1 : 4).

The gas analysis agrees well with the equations (1) and (2) (allowing for $\frac{1}{2}$ mol. CO_2 from the reaction of acetic acid with the $CaCO_3$ present), but the alcohol-acetic ratio should be 3 : 4. However, as there is always some free and combined oxygen (sulphates) present it is quite possible that $CH_3 . CHO$ is oxidised directly to $CH_3 \cdot COOH$.

(4) The products of fermentation generally weigh more than 110 per cent. of the cellulose fermented.

As regards equation (3), it is invariably my experience that whenever CH_4 appears in the gases, alcohol either ceases to be produced, or, in many cases actually disappears and the acetic acid yield increases proportionally. In some cases alcohol has disappeared from a culture without an appreciable attack on the cellulose. The gases then contained about 30 per cent. CH_4.

As regards equation (4), according to equations (1) and (2) (see above), the highest alcohol : acetic acid ratio should be 3 : 4, i.e. 46 : 60. However, it often happens that the ratio rises to 2 : 1, at the same time the evolved gases approximate to CO_2 75 per cent., H_2 25 per cent.

It has also been established that under the fermentation conditions with excessive aeration, alcohol and acetic acid are completely oxidised to CO_2 and H_2O.

A compound with the physical characteristics of glycerin or lactic acid may also be obtained in very large yield under certain conditions. It has been assumed to be lactic acid for the following reasons :—

(1) Non-volatile at 100° C.

(2) Gives a good yield of acetic acid with CrO_3 mixture with acetaldehyde as intermediate product.

(3) Gives high yield of oxalic and with alkaline $KMnO_4$.

Estimated in terms of oxalic acid by oxidation with alkaline $KMnO_4$ and calculated as lactic acid, yields of 30 per cent. on the cellulose fermented have been obtained.

In the absence of a specific method of determining the residual cellulose in a culture, the organic matter, insoluble in water, is taken as cellulose. There may here be an error (5 per cent.) due to inclusion of bacteria.

On the basis of the above deductions and hypotheses, the typical results are as follows, per cent. : —

	Wood cellulose, sulphite pulp.	Megass 'cellulose,' residue from NaOH digestion.
Acetic acid	31·8	74·6
Lactic acid	9·6	2·2
Alcohol	27·6	—
Gases $\begin{cases} CO_2 \\ H_2 \\ CH_4 \end{cases}$	42·4 1·0 0·2	27·8 0·2 8·0

The CH_4 figures are liable to be low owing to explosion over water in analysis.

The acetic acid gives a combining weight of 62 to 64.

The alcohol is estimated by distillation and oxidation with dilute CrO_3 mixture in closed bottles at 100° C. for two hours. The remaining CrO_3 is determined volumetrically, and checked by estimating the acetic acid produced. Its combining weight is calculated from Ag salt, 62 to 64.

*　　*　　*　　*　　*　　*　　*

The Paper and Textile Industries, which involve a large number of problems of the special chemistry of the fibre colloids have not shown any marked changes from the treatments fixed as routine standards at the time of our last volume (1910). The paper-making industry is investigating more specifically the hydration effects which are a necessary condition of the preparation of pulps for working on the machine. These effects are known to be a direct function of the beating process, and some inventions have endeavoured to intensify these actions by special means—the Jackson Beater with its centri-

fugal hammers and the Arledter Beater (1913) which employs the device of vacuum pressure as auxiliary treatment, have claimed serious attention, but for economic reasons have not been adopted. It will be evident from our previous discussion of hydration effects that there is considerable scope for investigation of this complex effect of full colloidal hydration, as of its stages, especially in relation to the contributory effects of physical mechanical agencies.

Towards realisation of this forecast, and during the printing of this work, Arledter has constructed a Beater embodying the principles of a recent series of Patents, and one of us, with S. Milne of Bertrams, Ltd., Edinburgh, has been engaged in a systematic investigation of the invention, that is, of the machine, from the point of view of power consumption in relation to effect, and of the process from the point of view of the mechanical-physical-chemical agencies involved.

Some remarkable effects are obtained, and in both aspects ; the machine works with great efficiency and economy in regard to the time-power factors (H.P.H.), and produces effects in preparation of pulps for working into paper, which are in advance of anything obtainable in the ordinary Hollander, or in any perfected Beater of the ordinary type.

The vacuum principle is utilised in the mechanism of circulation ; but the intensification of the beating preparation appears to involve several factors, both of mechanism and construction, and of physical effects, in which rapidly alternating pressure volume changes are involved. The matter is under investigation from two points of view : (1) That of accepted theories of the Beater and Beating process, of which we have a lucid exposition in 'Die Rationelle Theorie des Ganzzeng-Holländers,' by Dr. Sigurd Smith (Charlottenlund, Denmark, 1919 : Berlin, 1921) ; (2) that of the present volume, and especially of the researches on the relation of Cellulose to mechanical force and other forms of energy.

The more special technical features of the results obtained are acceleration of the hydration effects, and conservation of the fibres under the action of the beater roll.

In applying this beater to the preparation of half-stuff hydrated by chemical reaction as described on p. 104, a further range of effects is obtained.

In the textile industry we note a development of bleaching processes as applied to flax and cotton goods resulting from the studies of S. H. Higgins and others, on the advantage of a preliminary treatment with solvents for the removal of oil-wax-resin constituents of the fibre. Special advantages are claimed in regard to response of the fabrics so treated to the ordinary finishing operations : mangling, calendering and beetling. The reader is referred to a recent publication (Higgins, ' Researches on Bleaching,' 1922).

In all these industrial processes the colloidal characteristics of the fibre substance play an important part, and there is little doubt that the art and craftsmanship involved in these industries depends upon the perceptive realisation of such effects. It has been shown in these pages that the widest range of colloidal effects can now be controlled by treatment, and the economic industrial development of such effects is being actively pursued.

As a colloid, we have selected for special study the hemicelluloses of the locust bean. The hard parenchyma of these and indeed other seeds, is directly peptised by treatment with water. An industrial product known as tragasol has been specially developed by the Tragasol Manufacturing Co., of Hooton, whose technical publications are well known in the dyeing and finishing and the leather trades. A particular application of these characteristic colloids resulted from investigations which are set forth in the following paper given as published :—

COLLOIDAL TANNIN COMPOUNDS AND THEIR APPLICATIONS.

C. F. Cross, C. V. Greenwood and M. C. Lamb (J. Soc. Dyers and Col., 1919, **35,** 62).

It is generally recognised that human industry is in large part a further phase or development of processes of the natural world, and that the raw materials of industry are also, in large part, natural products, the properties and qualities of which are its conditioning factors, as they are of the applications and uses of its products. The industries based upon organic products are largely concerned in the fashioning of these into fabrics, for which the raw materials are the structural forms of organised matter—animal and vegetable.

These raw materials are colloids, and hence the technology of our more important industries of this group, (*a*) the textile arts, including twine and rope-making, paper-making, (*b*) leather, (*c*) rubber manufactures, are based on the mechanical-physical-chemical properties and reactions of colloidal matter as such.

Since the specialised study of phenomena and reactions in this field is relatively recent, the industrial arts of which they are the prime factors have been elaborated to a high grade of perfection, independently of formal science.

In applying to these arts the formal criticism of later birth, we find very much to appreciate and justify in the light of more exact knowledge ; in many cases, on the other hand, we find that empiricism has devoloped prejudice, and that the prejudice is the more deeply rooted because it reflects fundamental features of colloid phenomena. There are two groups of factors particularly involved in this aspect of industry : (1) the time factor. Thus, it requires many weeks to carry through the bleaching of fine linen goods ; it takes months to produce a pit-tanned sole leather of standard quality ; and years to

'season' a timber for special structural applications. (2) The life-history factor. The natural structural colloids have their individual characteristics, but a uniformity which masks extreme underlying variability ; or in another aspect, a highly resistant aggregate quality, associated with extreme reactivity of component groups.

As the subject of this communication is sectional, we limit the consideration of these factors to their incidents in the leather industry.

The two factors are associated in their effects for the reason that the skin-substance is highly reactive and changing throughout the period or duration of the entire process of conversion to leather, as of each of the succession of treatments.   It may be, therefore, that in attempting a quick tannage, by applying a certain principle to control the main reaction between the collagen and tannins, we may disturb the system in respect of secondary reactions, the results of which are factors of leather quality.

Any question of this order is decided by a test of quality, of which the standard is one of empirical recognition and definition.   There cannot, in the nature of colloidal things, be the one 'ideal' leather, for that would admit of comprehensive exact definition.   Our knowledge of leather, as of its antecedent forms, is incomplete in important details, therefore inexact.   Hence the empirical standard is a standard of science, but with the reservation that with progress of exact knowledge it may yield to one more nearly approximating to an ideal.

We have to give an account of progress in the application of a technical principle, shortly expressed as 'restrained tannage.'   It is well known that the collagen-tannic acid reaction is of the rapid or violent order, and hence a dehaired and purified skin, plunged into a strong solution of tannic acid, would react by strata, the reaction product of the external stratum, opposing the penetration of the reagent ; hence a

stratified agglomerate, the last antithesis of a uniformly con-
verted leather. This reaction is controlled in the established
practice of pit tannage, by graduated treatments of increasing
concentration of active tannin constituents.

Another instance from technical practice of strong reaction-
affinity, requiring control, is that of the dyeing of silk, especially
with the modern synthetic products. In this case a certain
control and regulation would result from treatment with highly
dilute solutions (in water) as dye bath, but not sufficiently to
meet all the exigencies of skein dyeing in mass. This, however,
is secured by the use of a mixture of emulsion colloids, the silk
degumming liquors, neutralised with acid, giving an emulsion
mixture of silk-gum solids and fat acids (from the soaps em-
ployed) with neutral alkali salts in solution. These liquors
suitably diluted as a dye reaction bath convert the dye com-
pounds when added into emulsion compounds, from which
they are withdrawn by the silk substance, subsequently entered,
as a differential reaction, controlled, that is, by the (lesser)
affinity of the mixed hydrated colloids of the special bath.

In the course of investigations on the hemicelluloses of
seed endosperms, the basis of the well-known tragasol prepara-
tions, we had occasion to study their compounds with tannic
acids, which may be produced under carefully regulated con-
ditions as homogeneous reversible gels, closely resembling in
'colloidal habit' a gelatin gel of 3 to 5 per cent. gelatin.
With practical experience of silk dyeing methods, and taking
into account the above noted relations of the water temperature
equilibrium of the hemicellulose-tannin colloid, we were im-
pressed with a probable solution of the technical problem of
quick tannage in terms analogous with that of silk dyeing, the
hemicellulose-tannin compounds functioning as the intermediate
controlling form of the specific active reagent. After many
days of difficulty, the incubation period common to all technical
progress, we have to note the *fait accompli* with some details of

results.   For a general outline of the physics and chemistry of
these hemicelluloses and their tannin compounds, we refer to
'Cellulose,' *Inst. Chem. Lecture*, C. F. Cross, and to *B.A.
First Report on Colloid Chemistry*, 1917, article, H. B. Stocks.

In the technical applications of the hydrated forms of the
hemicellulose of the endosperm as 'tragasol' gums, much study
has been involved in the fixing of standard types, and of the

Viscosity of Tragasol Solutions.

Time of flow in seconds.

Temperature.
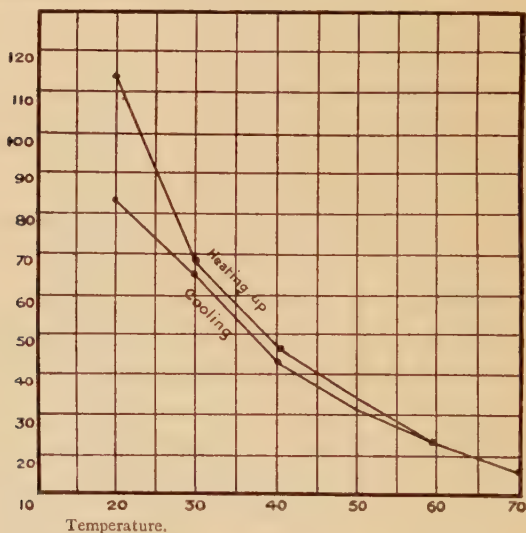
FIG. 12.

further treatment of the standard products in their various
applications.   The results are embodied in the technical pub-
lications of the Tragasol Co., but without reference to the
methods of investigation by which they have been fixed.

Certain of these are important in the technical control of
processes of application, such as the methods of tanning about
to be described, and, for the benefit of workers who aim at
technical progress, we mention them in brief outline.

Viscosity.—The time out-flow method is convenient; for more exact comparisons the basis should be the percentage of 'dissolved' solids of the 'gum.'

The following types may be noted, showing the relation of viscosity as thus measured : (1) to total solids, (2) to temperature (heating and cooling).

It will be noted that 'specific viscosity' increases with dilution. This is no doubt correlated with increase of specific density, which we may presume obtains in the case of these hemicellulose colloids (Cross and Bevan, *J. Soc. Dyers and Col.*, 1918, **34,** 217), and both effects are no doubt correlated with reduction of dimensions of ultimate component groups.

In regard to technical control of quality, the following observations on standard commercial preparations illustrate the change of viscosity with age, i.e. on keeping at ordinary temperatures :—

			Per cent. solids.	As received.	Nine days old.	Sixteen days.	Twenty-three days.
Mark *a*	.	.	0·50	242	242	155	138
,, *b*	.	.	0·47	274	168	164	160
,, *c*	.	.	0·44	232	210	185	165
,, *d*	.	.	0·43	143	88	76	75

Viscosity. Seconds of outflow water = 39.

Diagnosis of the Hemicellulose.—Adopting the current view of a mannan-galactan complex, the hydrated forms of which constitute the 'tragasol' gums, the progress of hydrolytic resolution incidental to original preparation and to keeping as a 'gel' of 3 per cent. solid contents, is marked by reduction of viscosity, transition from pseudo-solution to true solution, and, lastly, the appearance of cupric-reducing bodies.

A useful method of diagnosis is based on the reaction with Fehling's solution, which gives (*a*) in the cold, a blue gelatinous coagulum, (*b*) in the filtrate from (*a*), reduction (to Cu_2O) in the case of gums in more advanced stages. The CuO precipitated in (*a*) and the Cu_2O in (*b*) are obviously measures of constitutional features of the carbohydrate complex. For

rapid quantitative estimation, to 100 c.c. of gum, 20 c.c. of Felhing's solution are added with vigorous stirring—the precipitate is filtered through a plug of glass wool—the filtrate divided into two portions: in one, after acidification, the Cu is estimated by iodometric method; the other is boiled, and the ppt. of Cu_2O estimated as in 'sugar' titrations.

The following results are typical:—

(1) *Acid Hydrolysis* (1 per cent. H_2SO_4, boiling) of tragasol gum (1·5 per cent. solids)—

	Cu_2O equivalent to hexose.		
Original.	Fifteen minutes.	Thirty minutes.	Sixty minutes.
0·0	6·8 per cent.	9·0 per cent.	13·8 per cent.

(2) As above, but time constant (thirty minutes), H_2SO_4 varied—

H_2SO_4.	(Viscosity. $H_2O = 39$.)	CuO in ppt. (cold), as Cu per cent. solids.	Cu_2O ppt. (boiling), calc. to hexose per cent.
0·10	58	8·97	trace
0·25	44	8·42	trace
0·40	40	8·42	2·00
0·50	40	9·44	2·00

(3) *Hydrolysis due to Mould and Bacterial Growth.*—This was a specimen of original hydrated 'splits,' i.e. endosperms kept sixteen days at ordinary temperature.

It gave 69·9 per cent. solids *in filtered solution*. The following constants were determined:—

	Per cent. of solids.
Cu as CuO in ppt. (cold)	11·17
Cu_2O reduced (boiling) calc. to hexose	9·08
Galactose (groups) from mucic acid in HNO_3 oxidation .	13·7

(4) To compare with this 'natural' process, a specimen of original material was hydrolysed with 1 per cent. H_2SO_4, and the solution gave:—

Cu as Cu_2O in ppt.	8·02
Cu_2O calc. to hexose	5·7
Galactose (calc. from mucic acid)	14·4

(5) The original material, on the other hand, subjected to intensified 'natural' process, viz. four days' incubation in hydrated condition at 35°, gave another type of hydrolytic resolution, the solution giving :—

Cu as Cu_2O in ppt.	4·63
Cu_2O calc. to hexose	18·10

These illustrations are a sufficient *exposé*, without discussion, of the value of the method in diagnosing the general constitutional features of these hemicellulose gums.

There are, moreover, definite correlations of these constants with those of the hemicellulose-tannin reactions.

As the hemicelluloses break down under hydrolysis, so the precipitates with tannic acid tend to the flocculent, free form, and away from that of a coherent homogeneous coagulum, i.e. the reversible 'gel' form. It will also be evident that with the extremely variable forms of the characteristic tannins of the industrial raw materials and prepared extracts, there are corresponding variations in the 'colloidal habit' of the precipitates which they give with the hemicelluloses.

To discuss this wide range of diversified variations would take us outside our prescribed limits. The question of the reciprocal incidence of the hemicellulose-tannin reaction is obviously one which requires extension on the side of the latter.

Structural Quality of the Hemicelluloses.—The hemicelluloses are characteristic components of seed tissues, notably of endosperms, and in the dense compact form in which they are elaborated, they constitute a rigid solid. The hydrated hemicellulose, when reconverted to solid in the form of a translucent film, has been tested from time to time for breaking strain. We have calculated the data into the form which places the tragasol film-solid into direct comparison with other organic colloids and derivatives, as well as with fibrous aggregates, e.g. papers or textile fabrics.

The figures range from—

Breaking length.				Elongation at break.
5300 to 8870 metres .	.	.	.	5 to 7 per cent.

which indicate a high order of agglomerative cohesion.

It is to be noted that the films have a psuedo-fibrous structure, due to the expansion and drawing out of the cells in the distended hydrated forms in which they constitute the tragasol pseudo-solutions.

In proceeding to a brief account of practical work in leather production based on the application of these hemicelluloses, we note that the technical problems of this industry are formally adopted into the general system of colloid phenomena, of which they are important illustrative sections (*B.A. Report*, 1917, H. R. Proctor ; *Colloid Chemistry*, F. Tanning).

It appears, moreover, that investigations have so far been concerned rather with the auxiliary treatments of the hides than with the primary collagen-tannin reactions, and that the action of colloids in the processes of the leather industry has passed into practice without critical examination. Adding the new factor to these may prove of some assistance in the general elucidation.

From experiments on a small practical scale, it was found that the theoretical inferences above outlined were confirmed by results.

Thus, a tanning liquor made up with equal weights of quebracho extract, containing 25 to 29 per cent. tannins, and tragasol gum, each previously diluted and mixed with all the precautions necessary to maintain the colloidal hydration at a maximum, was employed upon prepared pelts, with the result of producing a leather entirely free from the defect of case hardening.

Given the general idea of a vegetable tanning agent rendered sufficiently colloidal by admixture with the tragasol hemicellulose, to ensure the tannage being restrained to such a degree as to exclude case hardening, the tanner has the choice of

several methods of application. Up to the present the practical application of the tragasol tannin complex has, in the main, been confined to the tanning of sole and dressing leather.

The methods of application may be classed as follows :—

(*a*) Placing the previously delimed and washed goods in a pit or vat immersed either laid flat or suspended in the tragasol-tanning extract mixture, handling the goods occasionally, and strengthening the mixture by the addition of further tanning extract, to replace the amount absorbed by the goods. The goods 'strike through' with great rapidity, as compared with the tanning process with aqueous solution of the tanning material, and complete permeation can, if desired, be encompassed in two to three days, even in the case of the thickest hide. It will generally, however, be found advantageous to allow a longer time to elapse before removal of the goods in order to ensure a thorough tannage by more complete combination with the nitrogenous colloid of the hide.

If on removal of the tanned goods from the mixture it is desirable, with a view to obtaining greater weight and solidity than is effected by simple conversion into leather, the ordinary practice of placing the goods into 'lay-aways' with liquors of 100° to 150° Barkometer may be adopted, or the goods may be rinsed, drained, and placed into warm tanning extract.

(*b*) If desired, the tannage may be carried out in the drum or Wilson tanning machine, taking the goods from about half-way up the suspender round, and feeding into the drum a liquor of about 75° Bark., to which about 30 per cent. tragasol (calculated on the weight of goods) has been added, drumming intermittently for about thirty-six hours, when the goods will be completely penetrated, and can subsequently be weighted by vatting, laying away, or drumming, in concentrated extract.

(*c*) A further method of application which is being practised successfully is to drum the goods after deliming and rinsing, in the strong colloidal tragasol jelly, using some 30 to 40 per cent.

of the mixture on the weight of delimed hide, drumming for two to three hours until the goods have become thoroughly impregnated, and then either transferring to a pit containing strong extract, or making the addition to the goods in the drum.   By this method the interaction between the tragasol and the tannin takes place within the goods themselves.

Whichever method of application is adopted, it will be found in every case that the finished goods possess a fine smooth-textured grain surface by comparison with that ordinarily obtained, and there is an absence of the graining usually noticeable on goods which have been drummed.   Furthermore, the filling of the interstices of the hide with the colloidal gel has the effect of producing a leather possessing a greater plumpness in the flanks and thin portions than is generally associated with a leather tanned in the aqueous semi-colloidal infusions usually employed.

Owing to the viscous colloidal state of the tanning mixture the leather is in some measure protected from the action of air in the tanning process, with the result, due to the lesser oxidation of the tannins, that the colour of the leather is much whiter than when the goods have been tanned by the ordinary methods of long duration.

In regard to the important question of weight of leather produced by this method, it is, as in ordinary tanning practice, a very variable ratio, and dependent upon (*a*) the particular variations of method adopted, and (*b*) the tanning materials employed.   It may be said, however, that the weights bear favourable comparison.   The following may be quoted :—

Weight of hides.	Rounding table weight.	Crust tanned weight.	Per cent. crust tanned on weight of hide.	Per cent. crust tanned on rounding table weight.
lb.	lb.	lb.	lb.	lb.
67	30	22·6	33·7	75·3

The tragasol complex being only semi-soluble in water, it follows that leather tanned by the restrained method, having its interstices filled with the colloidal complex, possesses water-resisting properties not common to the average leather tanned by ordinary processes.

An analysis of tragasol-tannin leather gave the following figures :—

Hide substance	34·94 per cent.
Tannin and organic matter . .	46·68 ,,

which bears most favourable comparison with a good tannage of the West of England standard, giving :—

Hide substance	39·6 per cent.
Tannin and organic matter . . .	45·5 ,,

So far, in dealing with the leather problem, we have kept to a technical description and *exposé*, and in considering an extension of the general principles, we will continue on technical lines in dealing with the two other types of leather processes. One particular example of such action and process which further illustrates the restraining influence of colloidal masses is seen in the alum, salt, flour, and egg-yolk mixture employed in the tawing of glove leathers. This process may be cited as the only one in practical use where the tanning agent, sulphate of alumina, is used at such strength at the commencement of the leathering operation that no further addition is necessary to complete the tanning of the goods under treatment, the colloidal condition of the mixture, due to the presence of flour and the yolk of egg restraining the otherwise too rapid action of the alum with its attendant liability of producing a 'drawn grain' leather.

In relation to the important modern development of chrome tannage, some recent experiments have indicated the advantages of employing the hemicellulose in association with

solutions of chromium salts in the chrome tanning of sole leather, belting, hydraulic leathers.

It is well understood that it is desirable in the production of chrome leather that the finished leather should possess a moderately high chromic oxide content, and in the tannage of chrome sole leather that the pelt should be kept in as plump condition as possible, in order to ensure the production of a stout full leather.

Tannage in a colloidal complex of hemicellulose and basic chromium sulphate effects both of these desired results.

The following figures were obtained in the tanning of two packs of bends, (*a*) in water solution, (*b*) in colloidal mixture :—

	Water solution.	Colloidal mixture.
Percentage yield on rounding table weight	42·3	55·9
Percentage chromic oxide .	3·175	3·5

In the tanning of the two packs of goods, the factors of reaction, except as regards the modification of the colloidal condition of the bath, were kept absolutely identical, i.e. in respect of basicity and proportion of chrome sulphate solution, duration of immersion, and temperature.

Whereas the tannage in aqueous solution was only effected after some four days' immersion, the tannage in the colloidal chrome gel was observed to be complete in twenty-four hours, but in order to maintain the basis of comparison, the goods were allowed to remain in the bath for the period required to complete the tannage of the pack of goods processed in the aqueous solution. The greater thickness noticeable in the finished leather would appear to be accounted for by the fact that the hide being immersed in the colloidal gel, the individual fibres are kept in a more plump and swollen condition than when under the action of the aqueous solution in which they tend to shrinkage and collapse ; the plump condition of

the fibres is retained until fully penetrated by the chrome salt. In regard to the quality of the finished leather, there appears to be a certain filling up of the interstices between the fibres with the colloid, which influences the finish and the condition of equilibrium of the leather substance with atmospheric moisture.

In conclusion, we revert to the question of physical-chemical properties of the hemicellulose compound. As stated, the precipitate formed on adding tannic acid to tragasol gel represents a reaction in the ratio $2C_6H_{10}O_5$ to $C_{14}H_{10}O_9$, but in regard to the reaction when mixed in this ratio the precipitation is incomplete. On gradually increasing the tannic acid to the double ratio we get the characteristic effect of the coagulum which is coherent, and shrinks in the vessel, fully retaining the form of the latter.

This observation is confirmed by a test of viscosity under the conditions of fractional addition to tannic acid of tragasol gel at a temperature of $45°$ C., which is well above that at which precipitation takes place.

In the following series it will be noticed that the maximum viscosity is attained with a 2 mol. ratio, and maintained up to a 4 mol. ratio.

$2C_6H_{10}O_5$	$C_{14}H_{10}O_9$	Seconds.	
1	0·2	14	(pure glycerine at
1	0·5	16	$45°$ C. 36 sec.)
1	1·0	18	
1	1·5	18	
1	2	20 ·	
1	4	20	
1	6	10	
	Tragasol	14	

Now in regard to the reactions of the tanning process. It will have been observed from the quantities cited that the proportion of hemicellulose used is very much less than the

equivalent of this range of ratios. It therefore appears that the functions of the hemicellulose involve further factors. Observations on the large scale have shown that on the alternative system of drumming the prepared pelt, with a hemicellulose gel as a preliminary treatment, this gel is undoubtedly absorbed. In this there are two effects to be reckoned with : (1) a mechanical penetration of the collagen-fibre structure by the hemicellulose, and (2) a certain degree of surface adhesion or partial penetration of the hydrated fibre substance as a physical chemical effect, in which the acidic groups of the hemicellulose come into play.

In regard to the reactions of the tanning process the hemicellulose, like the skin substance, is amphoteric. We must assume that in reacting with tannic acid the precipitate is formed as a result of interaction with its more basic groups, and the new complex is necessarily acid. This complex reacting, in turn with the amino-groups of the collagen substance, causes a proportional migration of hemicellulose into the actual reacting area, which is then the region of exchanges between the collagen and tannin complexes.

As from the figures above we may infer that the undesirable reaction would occur when the proportion of tannic acid to hemicellulose exceeds five molecular proportions, it appears that the conditions of the practical process are such as to exclude any local accumulation in this ratio.

There is one other condition of reaction to bring into account in the mental picture, viz. the special relationships of the hemicellulose-tannin complex to water.

The hydration phases of these complexes are evidently closely similar to those of the collagen substances, and this is an evident factor of the restraining or controlling influence upon the reactions of which water is the general medium.

Without attempting a more comprehensive theory of the new or modified process, we have in this provisional rationale

defined the lines of future investigation to this end; and, further, the phenomena described in connection with the hemicelluloses suggest a basis of critical investigation of the general functions of 'non tans' in the water-soluble tannins and extracts, in regard to their varying efficiency.

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In concluding this review with the foregoing retrospect of progress in industrial developments, it should be remarked that we are fully sensible of its inadequacy, which, however, is a reflect on of the period through which we have passed. On the one hand, constructive evolution arrested by the upheavals of the Great War; and on the other, the technical-scientific world has been confronted with a wide range of problems, often requiring solution under the stress of urgency; many of these must rank as industrial, although the immediate object of investigation was to improve, perfect, or invent materials or processes required in war service. The records of these investigations are documents of obviously special value, and are only progressively liberated for publication as scientific contributions. At this date we note and call attention to certain positive results of the war, in attaching to the cellulose industries a large number of new workers and new organisations, whose primary aim is progress in science; and in inspiring a very definite education of public opinion as to the relative importance of 'cellulose,' and its industries, in the scheme of things.

It is important to say a word as to the future, and as a general conclusion from this present critical survey of research work.

The discovery of a specific synthetic derivative of cellulose at any time, carries the potentiality of a new industry, or of fundamental developments of established industry. The ether derivatives, discovered in recent years, carried such industrial promise, which, however, has not been realised. It must also

be said of the acetates that their industrial developments are partial and disappointing. In both cases it appears that the reactions of formation are attended with too much destruction, in the constitutional sense, of the cellulose system or aggregate. The primary effects involving affinities of the feebler order, the break-down of the cellulose is evidently due to the actions of the secondary reagents, the alkaline hydrates and sulphuric acid, which induce the respective reactions. On the other hand, there are reactions of cellulose involving these powerful reagents in the formation of synthetical derivatives, in which the characteristics of the original cellulose are conserved ; these are the xanthogenic (hydrate) esters, and nitric esters. The industrial application of these esters critically studied from this point of view, with attention to the obvious failure of the competition of the later rivals, viz. of the alkyl ethers to displace the viscose products, and of the acetates to displace the nitrates as the basis of plastic structural manufactures, suggest that the properties which condition these applications are directly bound up with some primary factor of the reactions of formation. In the case of the viscose cycle of reactions, a characteristic feature is the spontaneous reversion of the xanthogenic ester, in solution, to ' cellulose ' ; while this regenerated cellulose is different from the original normal, it represents a considerable survival of the qualities of a structural colloid. In the nitric esters as such, the properties which condition the manufactures and uses of ' celluloid ' are obviously those of the original cellulose ; the structural colloid is conserved notwithstanding the ' dilution ' of cellulose matter by the nitric ester groups. The completion of the cycle through the denitration process, to cellulose, is attended by secondary changes with loss of structural quality and resistance to reaction. The cellulose is degraded.

Reverting to the suggestion that these results and effects involve a primary factor of the original reactions of formation : it is to be noted that in the xanthogenic reaction, the specific

reagent, carbon bisulphide, is an endothermic compound, and that in the nitric ester reaction, investigation of volume changes, has at least indicated that the energy of the H-OH reactions is not entirely liberated.

It has been attempted to decide this point, in the case of the nitrates, by direct measure of the thermal constants of reaction. The investigations are, however, incomplete, and publication of the results is reserved; while, in the case of the 'viscose' reactions, the measurement of these constants is obviously beset with such extraordinary difficulties that no investigation has yet been attempted.

There remains our suggestion, or hypothesis, regarding the nature of cellulose which is supported, as we have shown, by certain facts and some indications. There are further, some points of evidence in the generalised consideration of the aqueous solutions of cellulose determined by electrolytes, such as zinc chloride and sulphocyanides (Williams). In these effects the specific characteristics of cellulose, in relation to electrolytic strain, are a determining factor, and the mechanism of the changes is that of reciprocal interaction of polar constituent groups. As a working hypothesis we have always taken this polarity of cellulose, both latent and active, as representing a primary feature of constitution, not to be reconciled with any of the systematic formulæ proposed for the assumed invariable chemical individual. In accordance with this view, the solution of cellulose in aqueous electrolytes is a process which, in re-distributing the energy of the complex, lowers or reduces it to the molecular form in which it may very well be represented by a systematic formula. The antecedent form is 'organic' cellulose, the degraded molecular forms are an infinite series of polyhexose-anhydrides of diminishing complexity, with progressive resolution by reagents, of which the acids are obviously the most powerful and radical in their attack.

In the case of the cuprammonium solution, the interaction appears to be specific, and the industrial applications of the solution, as of the cellulose regenerated, show that the cellulose complex is more fully conserved than when dissolved in concentrated solutions of saline electrolytes.

We have noted the sensitiveness of the cuprammonium solutions to oxygen and to light which offers a field of investigation of great promise towards the solution of the problem of actual constitution.

Lastly, and quite generally, the cellulose industries, and mainly those of textiles and paper-making, are fields of systematic investigation, full of problems, the solution of which requires the directing influence of positive working hypotheses of constitution. Without wishing to discourage any investigation, however limited or sectional in its aim, it appears that much of the technical literature does, in effect, disclose a narrow and empirical working basis ; hence the records of investigation are diffuse, if not confusing, as in the case of oxy-hydrocellulose reactions. It is the main purpose of this volume to contribute to the formation of critical scientific opinion ; at the same time to emphasise our experience that in the problems and aspirations of 'industry,' there are more suggestions of development of the main subject and object, which is always the *actual* 'cellulose,' than in the field of systematic chemistry, defined by laboratory methods, and limited to the establishment of a constitutional formula co-ordinate with generalised conceptions of molecular configuration.

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